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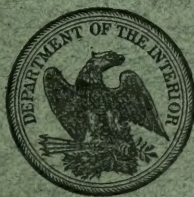
ESSENTIAL FACTORS

IN THE

FORMATION OF PRODUCER GAS

BY

J. K. CLEMENT, L. H. ADAMS,
AND C. N. HASKINS



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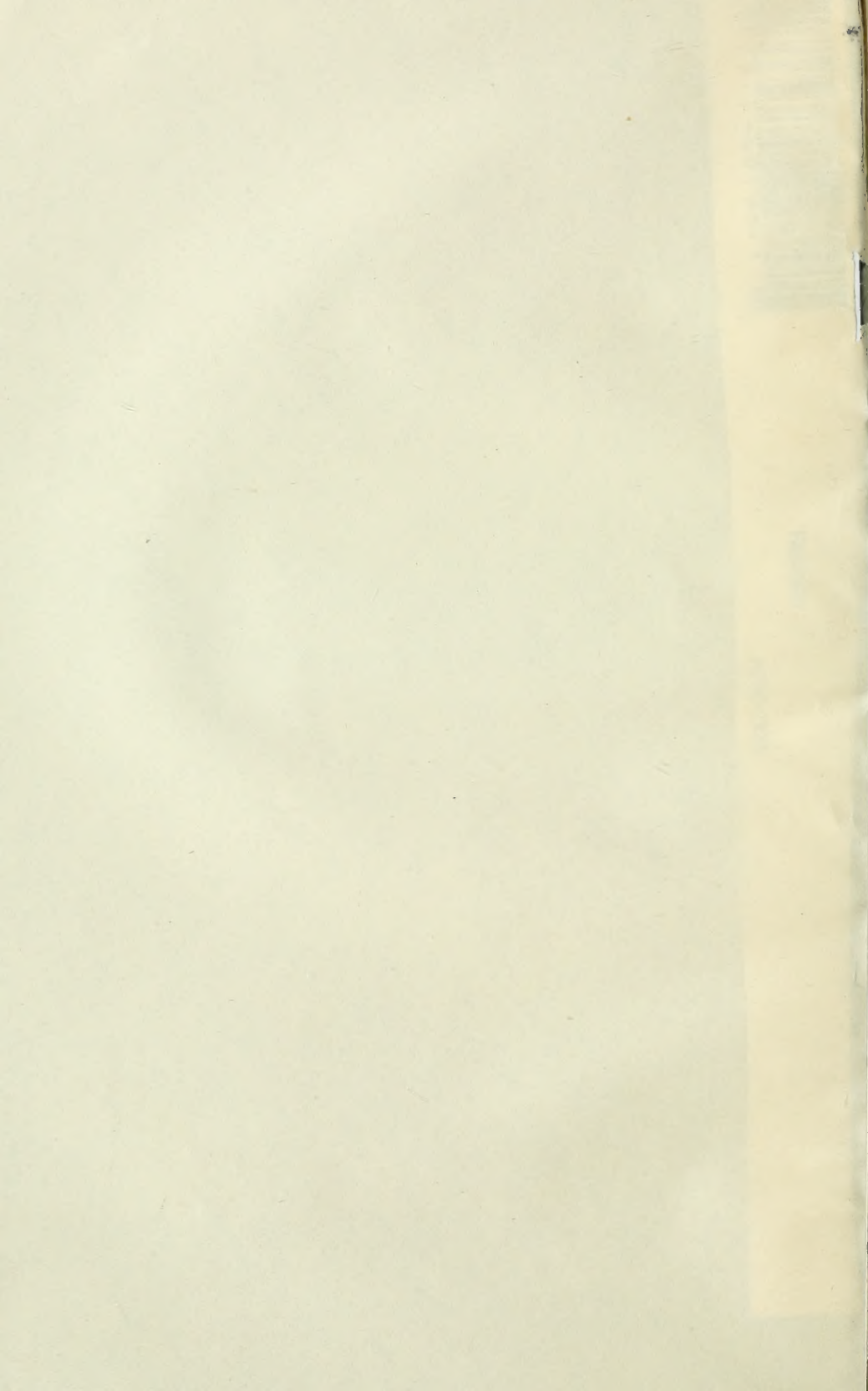
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ESSENTIAL FACTS
ON THE
FORMATION OF PRODUCER GAS



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Bulletin 7

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BUREAU OF MINES

JOSEPH A. HOLMES, DIRECTOR

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DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
GEORGE A. HODGES, DIRECTOR

ESSENTIAL FACTORS



IN THE

FORMATION OF PRODUCTION GAS

BY

L. K. FLEMING, L. H. ADAMS,
AND C. M. HARRIS



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ESSENTIAL FACTORS IN THE FORMATION OF PRODUCER GAS.

THE RATE OF FORMATION OF CARBON MONOXIDE AT HIGH TEMPERATURES.

By J. K. CLEMENT, L. H. ADAMS, and C. N. HASKINS.

EXPERIMENTAL INVESTIGATIONS.

By J. K. CLEMENT and L. H. ADAMS.

INTRODUCTION.

SCOPE AND PURPOSE OF INQUIRY.

In the course of its investigations of the fuel resources in the United States and of the methods by which these resources could be utilized with greatest efficiency, the United States Geological Survey tested a great variety of coals and lignites as gas-producer fuel. Early in these tests it was found that many factors controlling the formation of gas in the generating chamber of the producer and, consequently, having a direct bearing on the management of producer-gas plants, were not as well understood as they should be. The Geological Survey therefore took up a detailed investigation of the chemical and physical processes that take place in the producer, keeping in view not only the possibility of increasing the efficiency of the producer as a source of energy, and the ensuing benefits to the public of cheaper power and greater utilization of low-grade fuels, but also the application of the results to the problems of boiler-furnace operations.

The Bureau of Mines, to which the testing and analyzing of fuels as carried on by the United States Geological Survey has been transferred, is continuing producer-gas investigations at the testing station at Pittsburg, Pa. Results of the gas-producer tests^a made at the coal-testing plant erected at St. Louis, Mo., and of a study of some of the problems^b that came up in the tests have been published

^a U. S. Geol. Survey Bull. Nos. 261, 290, 332, and Prof. Paper No. 48.

^b U. S. Geol. Survey Bull. No. 393.

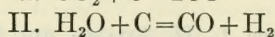
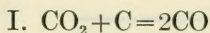
by the Geological Survey. Results of the tests made at Norfolk, Va., and Pittsburg, Pa., and of further studies of particular problems, will be published by the Bureau of Mines.

In the gas producer solid fuel is transformed into more readily combustible gaseous fuel. The transformation is relatively slow and consists of several processes:

1. The distillation of the volatile hydrocarbons from the freshly fired fuel at relatively low temperatures.

2. The combustion of the fuel by its combining with the oxygen of the air forming carbon dioxide (CO_2).

3. The formation of carbon monoxide (CO) and hydrogen (H_2), the essential constituents of producer gas, in accordance with the equations:



The reactions represented by these two equations are most important in the process of producer-gas generation, and it is with the first reaction that this chapter has to do.

In experiments made by one of the writers^a at the fuel-testing plant of the United States Geological Survey at Norfolk, Va., it was found that the temperature in the fuel bed of the gas producer varied greatly in different parts of the bed. In order to ascertain the conditions of temperature most favorable to the efficient operation of the producer, it became necessary to determine the temperature required for the formation of carbon monoxide and hydrogen in accordance with the above reactions.

Another reason for investigating the conditions for the reduction of carbon dioxide by carbon was that a small quantity of carbon monoxide is invariably contained in the flue gases of boiler furnaces and it was hoped that a means might be suggested of preventing its formation and the resulting loss in furnace efficiency.

BOUDOUARD'S INVESTIGATIONS.

An elaborate series of determinations of the amount of CO formed at different temperatures was made by O. Boudouard.^b The observations were made at temperatures of 650° , 800° , and 925°C . In his experiments at 650° and 800°C . glass tubes containing charcoal, coke, retort carbon, or lampblack were filled with CO_2 , heated to the desired temperature, and then sealed. The tubes were maintained at constant temperature until equilibrium was reached;

^a Clement, J. K., and Grine, H. A., U. S. Geol. Survey Bull. No. 393, 1909, pp. 15-27.

^b Boudouard, O., *Comptes rendus de l'Academie des Sciences*, vol. 128, 1899, pp. 824, 1524; vol. 130, 1900, p. 132; vol. 131, 1900, p. 1204. *Bulletin Soc. Chim.*, Paris, vol. 21, 1900; vol. 25, 1901; *Ann. de Chimie et de physique*, ser. 7, vol. 24, p. 354, 1901. See also Haber, Fritz, *Thermodynamics of technical gas reactions*, 1908, p. 311.

that is, until further heating at the same temperature produced no increase in the percentage of CO present. At 650° C. the heating was continued for 12 hours before equilibrium was attained. At 800° C. equilibrium was reached in 1 hour in the tubes containing charcoal and in 2½ hours in those containing lampblack. With coke and retort carbon the process was not complete at the end of 9 hours. In the experiment at 925° C. the carbon was heated in a porcelain tube, through which was passed a stream of CO₂. The average time of contact between CO₂ and carbon, calculated from the data given in Boudouard's account of his experiments, was approximately 30 seconds.

A summary of Boudouard's results is given in the following table:

Results of experiments by Boudouard on the formation of CO.

Temper- ature (° C.).	CO ₂ (per cent).	CO (per cent).
650	61	39
800	7	93
925	4	96

These values have been made the basis of computations by many writers on the chemistry of combustion and the water-gas reaction, and have been especially prominent in treatises on the gas producer.

In the first references ^a to Boudouard's work which came to the attention of the writers, no reference was made to the remarkably low reaction velocity of the formation of CO from CO₂ and carbon, and of the great length of time required to obtain the percentages of CO which are given in the above table. In at least one case the values given in the table were offered as representing the quality of the gas that should be obtained in the gas producer at the temperatures stated.^b The writers were, therefore, at first led to regard Boudouard's figures as defining the relative proportions of CO₂ and CO which should be formed in a gas producer at the various temperatures of the fuel bed, but such a view is quite erroneous, as the following experiments show:

EXPERIMENTS BY THE AUTHORS.

OBJECT OF EXPERIMENTS.

The experiments which form the theme of this chapter had originally as their object a critical repetition of Boudouard's experiments, and a continuation of them at higher temperatures. Preliminary

^a Haber, Fritz, *Thermodynamik Technischer Gas Reaktionen*. Munich and Berlin, 1905, p. 293. Fuchs, Paul, *Generator-, Kraftgas-, und Dampfkessel- Betrieb in Bezug auf Wärme-erzeugung und Wärme-verwendung*, 2nd edition, 1905.

^b Fuchs, loc. cit.

experiments, made by C. S. Hudson, demonstrated that the amount of CO formed at a given temperature depends largely upon the time of contact, or, in other words, on the rate of flow of the gas through the fuel bed. Apparently Boudouard's results represented the limiting values, which could be obtained only with a very low gas velocity. In order to ascertain the conditions for the formation of CO in producer furnaces, it was, therefore, necessary to determine the rate of formation of CO from CO_2 and carbon at various temperatures; that is, to determine the amount of CO formed with different rates of flow of the gas through the fuel bed.

APPARATUS.

Reaction tube and electric furnace.—The arrangement of the apparatus is shown in Plate I, and details of construction are given in figure 1 and figure 2. A porcelain tube of 1.5 cm. inside

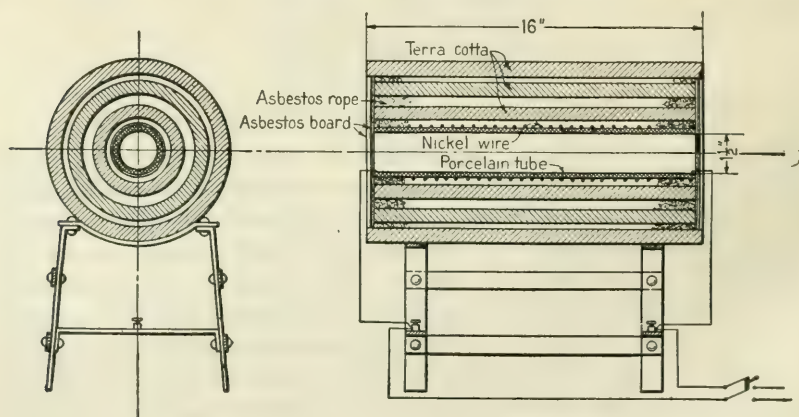


FIGURE 1.—Longitudinal and cross sections of electric furnace.

diameter, 60 cm. long, and glazed on the outside, was filled with charcoal, coal, or coke, and heated in an electric furnace (Plate I), which was designed especially for this investigation, and is shown in detail in figure 2. This furnace has been operated continuously

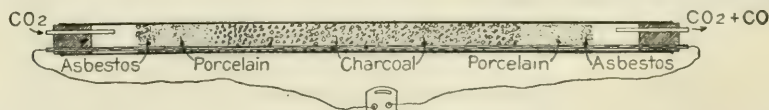
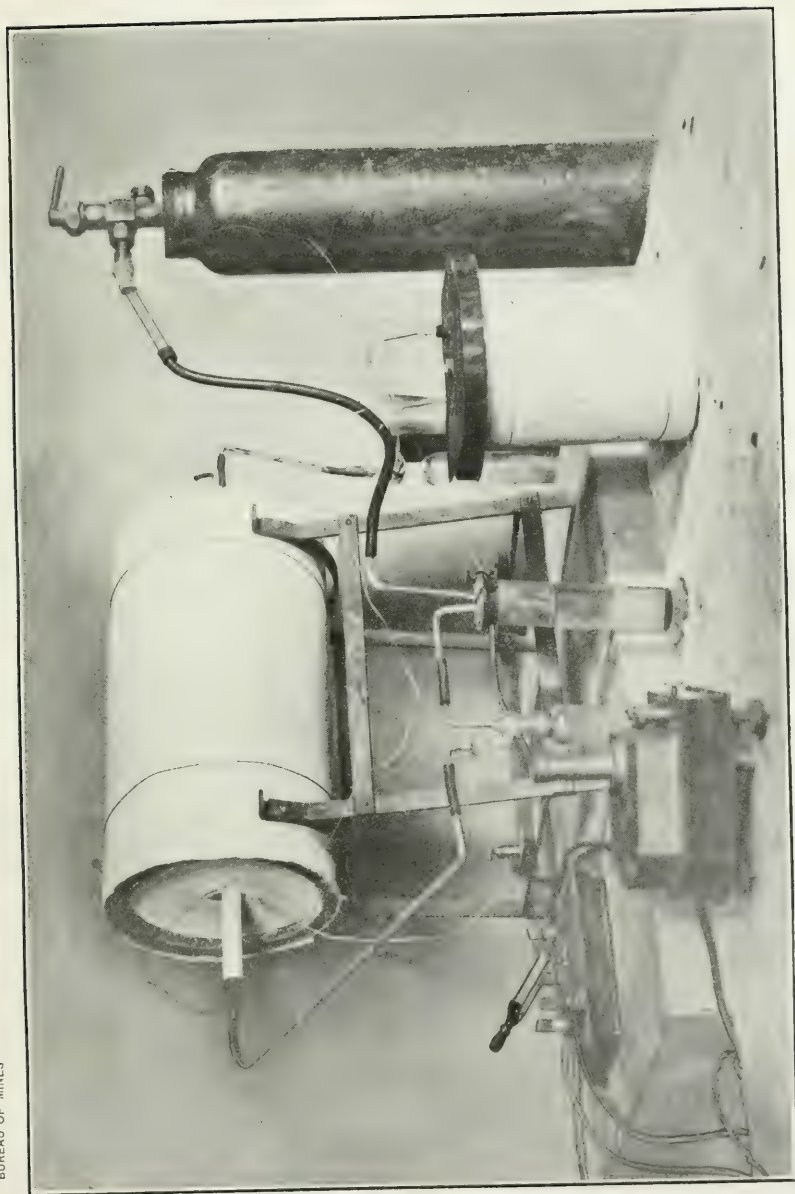


FIGURE 2.—Longitudinal section of reaction tube.

for a period of 6 months at temperatures of from 800° to $1,200^{\circ}$ C. and of even $1,300^{\circ}$ C. The temperature inside the porcelain tube can be maintained at any value up to $1,300^{\circ}$ C. with no fluctuations greater than 1° or 2° .

The heating coil is of No. 13 nickel wire, wound with eight turns per inch on an electrical porcelain insulating tube of 38 mm. inside



ELECTRIC FURNACE AND ACCESSORIES.

diameter and 35 cm. long. At either end of the coil the number of turns was increased slightly to compensate for the cooling effect at the end of the furnace. As a protection against corrosion the coil was painted with a thin layer of magnesite cement, a material capable of withstanding very high temperatures. The heating tube was then mounted inside of and concentric with three terracotta pipes, the spaces between the pipes having been filled with light calcined magnesia.

The cost of the materials used in the furnace and the amount of labor required were very small. The energy required to maintain a temperature of $1,000^{\circ}\text{C}$. was 600 watts.

Thermocouples.—The temperature inside the porcelain tube was measured by means of a platinum, platinum-rhodium thermocouple (see fig. 2), and a Siemens & Halske millivoltmeter. As the thermoelectric height of the couple fell slightly with use at high temperatures, probably because of the reducing action of CO on the insulating tubes and the consequent contamination of the couple, it was found necessary to calibrate the couple from time to time. This was done by determining the melting points of zinc, silver, and copper. The error of individual temperature observations does not exceed 5° below $1,100^{\circ}\text{C}$. nor 10° to 15° between $1,100^{\circ}$ and $1,300^{\circ}\text{C}$.

METHODS.

The carbon with which the porcelain tube was partly filled was crushed to pieces of a uniform size of about 5 mm. Only the middle part of the tube (see fig. 2) contained carbon, the remainder of the space being occupied by pieces of broken porcelain, which at one end served to heat the gas entering the tube, and at the other to increase the velocity of the gas through the region of falling temperature by reducing the size of the passageway. Through the porcelain tube was passed a stream of CO_2 . In the earlier experiments CO_2 was prepared from marble and hydrochloric acid; later it was taken from a tank of liquid CO_2 .

The velocity of the gas over the carbon was determined by the dimensions of the tube, the weight and density of the carbon, the temperature, and the volume of gas passed through the tube per minute.

The increase in the volume of the gas, due to the formation of two CO molecules in place of every molecule of CO_2 which disappeared in the passage of the gas through the reaction tube, made it difficult to determine accurately the time of contact, and consequently the velocity of the gas.

The values of t (the time of contact) given in the tables below are based on the volume of gas leaving the tube, and are therefore somewhat too low. Since most of the expansion takes place within a

short distance from the entrance to the tube, the error introduced is probably not appreciable.

The analyses were made by the Hempel method, both CO_2 and CO being absorbed. The amount of gas remaining in the burette after the absorption in cuprous chloride was seldom greater than 2 per cent.

EXPERIMENTS WITH CHARCOAL.

With the apparatus described experiments were conducted at temperatures ranging from 700° to $1,300^\circ$ C. The results of the observations with charcoal are contained in Table 1. The first and second columns of this table give the time of contact, t , and the reciprocal of the time of contact, $\frac{1}{t}$, which is proportional to the velocity of the gas through the fuel bed; that is,

$$\frac{1}{t} = \frac{\text{velocity of gas}}{\text{length of charcoal column}}$$

The third and fourth columns, respectively, give the quantity of CO, as observed and as calculated, in terms of percentage volume divided by 100. The values given for k_1 and k_2 are the respective velocity coefficients, at the particular temperature given, of the opposed reactions represented by the equations $\text{CO}_2 + \text{C} = 2 \text{CO}$ and $2 \text{CO} = \text{C} + \text{CO}_2$. For the method of calculation employed, the reader is referred to "Discussion of physical-chemical principles" (pp. 19-38).

A comparison of the results in Table 1, which are illustrated graphically in figures 3 and 4, shows, first, that with increasing temperature there is a rapid increase in the percentage of CO obtained with any given rate of flow of gas; second, that with increasing gas velocity the percentage of CO falls off very rapidly at low temperatures and very slowly at high temperatures. These variations are illustrated by curves in figure 3, in which the percentage of CO is plotted as a function of $\frac{1}{t}$.

TABLE 1.—Rate of formation of CO from CO_2 and charcoal.

AT A TEMPERATURE OF 800° C.

[$k_1=0.01968$. $k_2=3.031$.]

Time of contact, in seconds, t .	$\frac{1}{t}$	Per cent CO 100 observed.	Per cent CO 100 calculated.
∞	0		0.535
188.6	0.0053	0.503	0.534
115.9	0.0086	0.504	0.527
57.18	0.0175	0.518	0.508
45.70	0.0219	0.522	0.468
24.20	0.0413	0.375	0.345
15.50	0.0645	0.283	0.252
12.32	0.0810	0.245	0.209
2.686	0.354	0.063	0.051
1.550	0.645	0.039	0.030

TABLE 1.—Rate of formation of CO from CO₂ and charcoal—Continued.

AT A TEMPERATURE OF 850° C.

[$k_1=0.07174$. $k_2=3.238$.]

Time of contact, in seconds, t .	$\frac{1}{t}$	Per cent CO 100 observed.	Per cent CG 100 calculated.
∞	0		0.742
123.0	0.0082	0.743	0.742
54.18	0.0184	0.702	0.741
24.43	0.0410	0.572	0.694
13.23	0.0756	0.526	0.564
9.268	0.1070	0.297	0.463
4.630	0.216	0.297	0.281
3.686	0.271	0.224	0.231
3.254	0.307	0.225	0.207

AT A TEMPERATURE OF 900° C.

[$k_1=0.1540$. $k_2=2.599$.]

∞	0		0.873
64.29	0.0156	0.873	0.873
44.18	0.0226	0.867	0.872
10.008	0.0999	0.708	0.739
4.257	0.234	0.493	0.472
2.840	0.352	0.311	0.351
2.172	0.461	0.344	0.284

AT A TEMPERATURE OF 925° C.

[$k_1=0.2175$. $k_2=2.298$.]

∞	0		0.914
118.8	0.0084	0.947	0.914
81.2	0.0123	0.933	0.914
12.37	0.0807	0.848	0.875
5.80	0.1725	0.718	0.697
4.277	0.234	0.642	0.595
2.272	0.440	0.375	0.387

AT A TEMPERATURE OF 1,000° C.

[$k_1=0.6404$. $k_2=4.708$.]

∞	0		0.942
70.0	0.0143	0.949	0.942
18.60	0.0538	0.943	0.941
8.245	0.1195	0.903	0.938
3.675	0.272	0.797	0.869
2.296	0.436	0.795	0.752

AT A TEMPERATURE OF 1,100° C.

[$k_1=1.495$. $k_2=5.275$.]

∞	0		0.972
36.48	0.0274	0.987	0.972
10.43	0.0958	0.983	0.972
4.968	0.2010	0.981	0.971
3.640	0.2745	0.973	0.968
1.921	0.521	0.946	0.955

Since $\frac{1}{t} = \frac{v}{l}$, when l , the length of the charcoal column, is equal to 1, that is, equal to the unit of length, then the numbers along the $\frac{1}{t}$ -axis give the velocity of gas in terms of the same unit of length and

seconds. For example, the length of the charcoal column in the experiments here recorded was approximately 25 cm., or 10 inches. The velocity corresponding to the point $\frac{1}{t} = 1$, at the extreme right of figure 3, is, therefore, 10 inches per second.

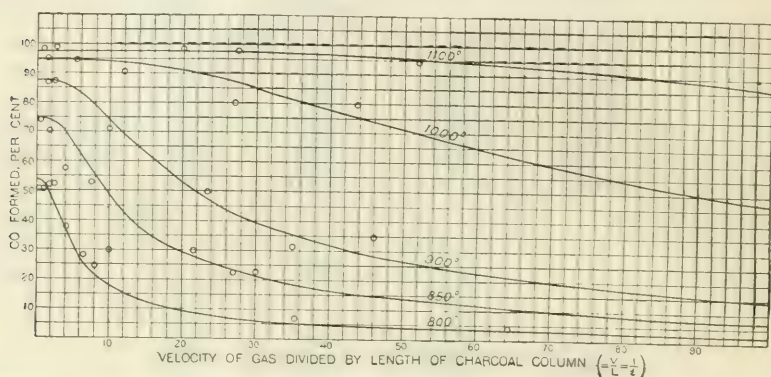


FIGURE 3.—Variation of percentage of CO formed from CO_2 and charcoal with change of gas velocity.

The curves through the points in the figure have not been arbitrarily drawn, but have been plotted from a mathematical equation, which expresses the percentage of CO as a function of $\frac{1}{t}$. (See "Discussion of physical-chemical principles.") The general shape of all the

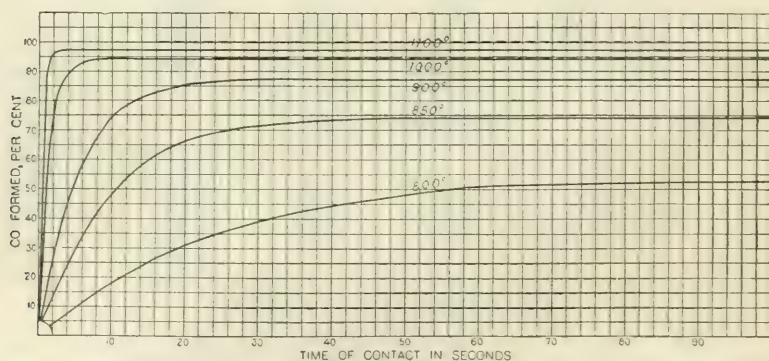


FIGURE 4.—Variation of percentage of CO formed from CO_2 and charcoal with change of time of contact.

curves in figure 3 is the same. The percentage of CO is greatest at zero velocity ($\frac{1}{t} = 0$, $t = \infty$). With increasing values of $\frac{1}{t}$, each curve falls away at first slowly, then more rapidly, passing a point of inflection, and, finally, becoming nearly horizontal. The intersections of the curves with the CO axis give the percentages of CO corresponding to the condition of equilibrium.

That a considerable amount of time is required to reach equilibrium in the reaction under consideration is further illustrated in figure 4, in which the percentage of CO is platted as a function of t , the time of contact. At 800°C ., for example, the percentage of CO reaches a practically constant value at the end of 50 seconds; at $1,000^{\circ}\text{C}$. in 6 seconds.

In figure 3 (p. 12) the curve for 800°C . falls off very rapidly with increasing rate of flow of gas. At this temperature the gas velocity must be exceedingly low to obtain the equilibrium percentage of CO. At temperatures below 800°C . equilibrium could not be reached with the lowest gas velocities which could be maintained. A great number of experiments were made at 700°C ., but the results were too in-

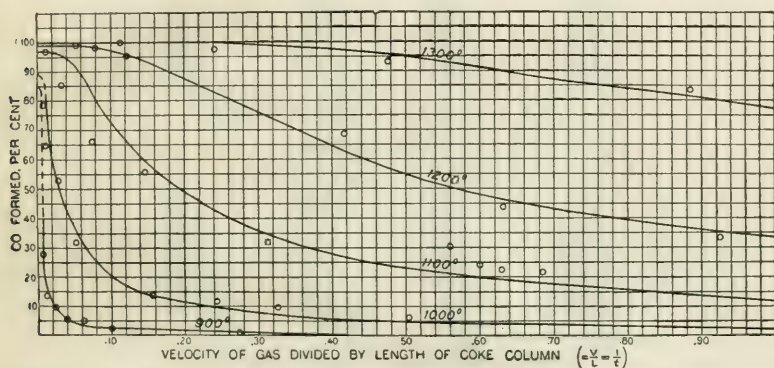


FIGURE 5.—Variation of percentage of CO formed from CO_2 and coke with change of gas velocity.

consistent to admit of mathematical treatment. Some of the observations are given in the following table:

Observations on the formation of CO from CO_2 and charcoal at a temperature of 700°C .

Time of contact, in seconds, t .	$\frac{1}{t}$	Per cent CO 100
99.9	0.0100	0.077
86.9	0.0115	0.012
86.2	0.0116	0.155
23.4	0.0426	0.004
15.0	0.0668	0.014
7.11	0.1405	0.009
9.71	0.103	0.022
5.60	0.178	0.006
5.02	0.199	0.008
4.18	0.239	0.012

These results show that, except at exceedingly low velocities, the amount of CO formed was never greater than 1 or 2 per cent.

EXPERIMENTS WITH COKE AND WITH ANTHRACITE.

The experiments with coke and with anthracite were conducted in the same manner as with charcoal. Table 2 contains the results of the observations with coke, while in figure 5 the same results are shown graphically.

The curves for 900°, 1,000°, and 1,100° C. are considerably lower than those for charcoal at the same temperatures except for very low velocities.

TABLE 2.—*Rate of formation of CO from CO₂ and coke.*

AT A TEMPERATURE OF 900° C.

[$k_1=0.00231$. $k_2=0.03686$.]

Time of contact, in seconds, <i>t</i> .	$\frac{1}{t}$	Percent CO 100 observed.	Percent CO 100 calculated.
142.0	0.0070	0.276	0.278
80.20	0.0124	0.131	0.169
43.91	0.0228	0.094	0.096
24.82	0.0403	0.057	0.056
16.11	0.0620	0.049	0.037
9.575	0.1045	0.026	0.023
3.741	0.2671	0.008	0.009

AT A TEMPERATURE OF 1,000° C.

[$k_1=0.02323$. $k_2=0.3591$.]

123.2	0.0081	0.784	0.866
80.25	0.0125	0.644	0.795
33.25	0.0301	0.529	0.527
18.72	0.0535	0.320	0.350
6.37	0.1571	0.139	0.138
4.101	0.2439	0.115	0.091
3.072	0.3258	0.092	0.069
1.983	0.5045	0.063	0.045

AT A TEMPERATURE OF 1,100° C.

[$k_1=0.1335$. $k_2=0.5296$.]

90.00	0.0111	0.971	0.971
29.92	0.0334	0.854	0.955
13.20	0.0758	0.661	0.817
6.765	0.1476	0.556	0.592
3.198	0.3135	0.317	0.346
1.784	0.5606	0.304	0.211
1.660	0.6030	0.240	0.1942
1.590	0.6299	0.221	0.1190
1.462	0.6840	0.214	0.177
0.962	1.0399	0.133	0.121

AT A TEMPERATURE OF 1,200° C.

[$k_1=0.4095$. $k_2=0.6718$.]

18.92	0.0528	0.989	0.987
12.70	0.0788	0.978	0.983
8.250	0.1213	0.953	0.956
2.402	0.4160	0.685	0.624
1.582	0.6320	0.439	0.460
1.080	0.9260	0.335	0.357

AT A TEMPERATURE OF 1,300° C.

[$k_1=1.483$. $k_2=0.7313$.]

8.860	0.1129	0.999	0.997
4.149	0.2415	0.979	0.997
2.100	0.4760	0.932	0.955
1.130	0.8850	0.834	0.816

TABLE 3.—Rate of formation of CO from CO₂ and anthracite.

AT A TEMPERATURE OF 1,100° C.

[$k_1=0.119$. $k_2=1.410$.]

Time of contact, in seconds, t .	$\frac{1}{t}$	Per cent CO 100 observed.	Per cent CO 100 calculated.
34.20	0.0293	0.8780	0.912
9.370	0.1069	0.6010	0.657
5.415	0.1848	0.4770	0.472
3.301	0.3026	0.3020	0.322
2.439	0.4101	0.2650	0.251

AT A TEMPERATURE OF 1,200° C.

[$k_1=0.2374$. $k_2=0.1767$.]

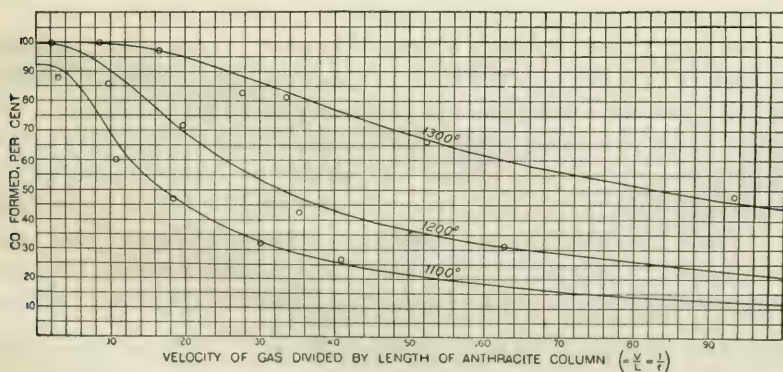
47.05	0.0212	0.997	0.993
10.39	0.0964	0.856	0.901
5.070	0.1971	0.715	0.688
2.845	0.3516	0.423	0.472
1.592	0.6270	0.310	0.309

AT A TEMPERATURE OF 1,300° C.

[$k_1=0.5791$. $k_2=0.2016$.]

12.40	0.0806	0.999	0.997
6.030	0.1659	0.965	0.968
3.600	0.2779	0.824	0.876
2.980	0.3358	0.809	0.822
1.908	0.5249	0.663	0.668
1.070	0.9350	0.503	0.462

The results of observations with anthracite are given in Table 3 and are illustrated graphically in figure 6. Here the curves fall off even more rapidly than those for coke in figure 5.

FIGURE 6.—Variation of percentage of CO formed from CO₂ and anthracite with change of gas velocity.

With very low velocities—that is, when the time of contact is sufficient for the reaction to reach equilibrium—the percentage of CO formed is practically the same with each of the three forms of carbon. The effect of the differences in the reaction velocities becomes more appreciable as the rate of flow of gas increases.

APPLICATION OF RESULTS OF EXPERIMENTS TO GAS-PRODUCER AND BOILER-FURNACE PROCESSES.

As stated in the introduction, the experiments here described were undertaken primarily to determine the temperature necessary for the formation of a gas containing a high percentage of CO in the fuel bed of the gas producer and to ascertain the conditions which govern the formation of CO in boiler furnaces.

FACTORS GOVERNING THE FORMATION OF CARBON MONOXIDE.

The results which are here presented indicate that the amount of CO formed in the gas producer depends on three factors—(1) the temperature, (2) the depth of the hot portion of the bed, and (3) the rate of flow of gas through the bed. To state it more concisely, the percentage of CO formed depends on the temperature and the time of contact of gas and carbon—that is, the average time required for a molecule of gas to pass through the fuel bed. The variation of the percentage of CO, with the rate of flow of gas, is illustrated in figures 3, 5, and 6. The curves for coke (fig. 5) may be taken as representing the conditions in the fuel bed of the producer. At $1,300^{\circ}\text{C.}$, for example, with zero velocity (time of contact $=\infty$), practically all the CO_2 will be converted to CO; when $\frac{1}{t}=0.5$ (time of contact, $t=2$ seconds), 90 per cent CO is obtained; and when $t=1$, only 80 per cent CO is formed. Since

$$\frac{1}{t} = \frac{\text{velocity of gas}}{\text{depth of fuel bed}} = \frac{v}{l},$$

in a fuel bed 1 foot in depth a time of contact, t , equal to 2 seconds corresponds to a velocity 0.5 foot per second, and a time of contact equal to 1 second corresponds to a velocity of 1 foot per second. At $1,300^{\circ}\text{C.}$, then, in a fuel bed 1 foot in depth, with a velocity of 0.5 foot per second, 90 per cent of CO would be formed, and with a velocity of 1 foot per second, 80 per cent would be formed; in a fuel bed 2 feet in depth the gas velocities corresponding to the same percentage of CO would be twice as great. In other words, for given conditions of temperature and quality of gas the depth of bed and velocity of gas must vary proportionally and their ratios $\frac{v}{l}$ must remain constant. A fuel bed 1 foot in depth and a gas velocity of 1 foot per second should yield the same percentage of CO as a bed 2 feet in depth with a gas velocity of 2 feet per second.

It is impossible to determine accurately the velocity of the gas through the producer fuel bed, because of the difficulty of estimat-

ing the magnitude of the passages through the bed.^a The velocity is probably between 0.5 and 5 feet per second. The right half of the curves in figure 5 lies within these limits, and therefore corresponds, approximately, to the conditions of producer operation.

Figure 7 shows graphically the variation in the amount of CO formed with rise of temperature at various values of $\frac{1}{t}$. The ordinate is the percentage of CO in gas initially containing 21 per cent CO₂ (air in which the oxygen has been converted quantitatively to CO₂). The abscissa is temperature in degrees centigrade. The upper curve for which $\frac{1}{t}=0$ represents the maximum amount of CO which could be produced from air. The intersection of the curve for any velocity with a given horizontal line—for example, the line for CO=30 per cent—gives the temperature required to form that

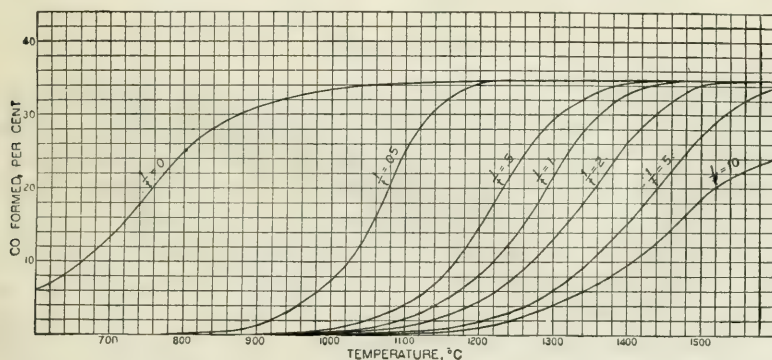


FIGURE 7.—Variation of percentage of CO formed with rise of temperature, using air and coke.

amount of CO with the particular velocity. Thus, to obtain 30 per cent CO with a velocity of 1 foot per second (depth of bed=1 foot) will require a temperature of 1,360° C., and with a velocity of 2 feet per second, 1,435° C. The curves of figures 5 and 7 indicate that the temperature of the producer bed should not be less than 1,300° C.

DISADVANTAGE OF AN EXTREMELY HOT FUEL BED.

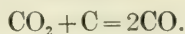
These investigations demonstrate that a very high temperature is necessary for the production of CO from CO₂ and carbon. There are considerations, however, which argue against operating the fuel bed of the gas producer at extremely high temperatures—above 1,300° C.

^a When any given number of pounds of air per second is passed through a fuel bed of given dimensions, the velocity through the bed will increase as the percentage of voids is decreased; e. g., the velocity will be much higher with slack coal than with uniformly sized nut coal. Further, the percentage of voids will be influenced by the amount of coking and clinkering.

A very hot fuel bed means that the gases will leave the producer at a high temperature, and thus lower the efficiency of the producer. The gain in capacity would, therefore, be accompanied by a loss in efficiency, unless the heat of the gases could be used for generating steam or preheating the air blast. A high temperature also favors clinkering. In the application of the results of these experiments to commercial producers and furnaces it will be necessary, of course, to consider the other questions which are involved.

CARBON MONOXIDE IN FLUE GAS FROM BOILER FURNACES.

Various explanations have been suggested to account for the presence of small amounts of CO in the flue gases of boiler furnaces. Perhaps the one most generally accepted by engineers is that the oxygen of the air first unites with carbon to form CO₂, and that as this gas passes up through the hot fuel bed it combines with carbon in accordance with the equation:



Assuming this to be the correct explanation, then the question to be solved is what conditions are favorable to this reaction and what conditions will tend to retard it. In the preceding paragraphs it has been shown that the higher the velocity of the gas and the thinner the fuel bed the less will be the percentage of CO formed. A heavy fuel bed in the boiler furnace would therefore favor the formation of CO. Also, the greater the supply of air to a given depth of bed the less should be the percentage of CO formed. These results show that with a hot fuel bed the formation of a small amount of CO is inevitable. In order that this CO may be burned to CO₂, it is necessary that in some way sufficient air be added to the hot gases as they leave the top of the fuel bed.

DISCUSSION OF PHYSICAL-CHEMICAL PRINCIPLES.

By J. K. CLEMENT, L. H. ADAMS, and C. N. HASKINS.

APPLICATION OF THE LAWS OF CHEMICAL EQUILIBRIUM AND REACTION KINETICS.

The velocity of a reaction in a homogeneous system is at any moment defined by the velocity coefficients and the concentrations of the various substances taking part in the reaction.

In heterogeneous systems, however, the reaction velocity depends usually on the rate of diffusion of the reacting substances, and on the area of the boundary surface between the two phases.^a

Nernst's^b theory, that in the boundary layer between a solid and a liquid phase equilibrium is established almost instantaneously and that the reaction velocity depends solely on the rate of diffusion, has been confirmed by Brunner^c in several cases. But, as Haber^d points out, the reactions which Brunner studied "involve merely the addition of a charge to substances going over into the ionic condition, and the loss of a charge by ions leaving the ionic condition."

Such changes universally take place instantaneously. Nernst's theory of the velocities of heterogeneous reactions applies when the chemical-reaction velocities are great compared with the rate of diffusion, but not necessarily when the reverse relation is met with.

Since the rate of diffusion of gases as compared to liquids is enormous, it seems quite possible that in reactions between solids and gases the rate of reaction may depend on the velocity of the chemical combination, as well as on the rate of diffusion. It is easily conceivable that the rate of diffusion may become so great compared with the reaction velocity that the latter becomes the determining factor. In this event the laws of reaction velocity which have been derived for homogeneous systems may be applied to heterogeneous reactions.

In the absence of any knowledge regarding the relative magnitudes of chemical-reaction velocity and rate of diffusion in any given

^a Boguski, *Ber. deutsch. chem. Ges.*, vol. 9 (1876), p. 1646. Noyes and Whitney, *Zeitschr. physik. Chem.*, vol. 23 (1897), p. 689.

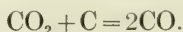
^b Nernst, *Walther, Theoretische Chem.*, 5th ed. (Stuttgart, 1907), pp. 578, 579; and *Zeitschr. f. physik. Chem.*, vol. 47 (1904), p. 52.

^c Brunner Karl, *Zeitschr. physik. Chem.* vol. 47 (1904), p. 56.

^d Haber, Fritz, *Thermodynamics of technical gas reactions*, London, 1908, pp. 253-254.

instance, the application of the laws of reaction velocity to a heterogeneous reaction can be justified only by the results obtained. If the velocity coefficients prove to be constant over a wide range of values of t (the time of contact), and if, further, the increase with temperature of the velocity coefficients is of the magnitude commonly observed in the case of homogeneous systems, then, in all probability, the determining factor in the reaction velocity is the velocity of chemical combination and not that of diffusion. The diffusion constants of gases vary according to the one and one-half to the second power of the absolute temperature.^a The latter value would correspond to an increase of 2.6 per cent for a rise of 10° at 500°C. , and of 1.6 per cent for the same rise of temperature at $1,000^\circ\text{C.}$ It will be shown later that the increase of coefficients of reaction velocity for the same rise of temperature should be about 20 per cent at 500°C. , and perhaps 10 per cent at $1,000^\circ\text{C.}$ ^b

The object of attempting to apply the laws of reaction kinetics to the results of the experiments described in "Experimental investigations" (pp. 7-15) was rather to obtain a means of interpolating and extrapolating the results than to furnish a confirmation of the laws themselves. The splendid agreement, however, between the observed and calculated values of the percentage of CO obtained with various gas velocities and the rapid increase of the rate of formation of CO with rise in temperature, argue in favor of the velocity of chemical combination as the determining factor in the speed of the reaction



THE EQUILIBRIUM CONSTANT.

It follows from the law of chemical mass action that in the heterogeneous system $\text{C} + \text{CO}_2 \rightleftharpoons 2\text{CO}$,^c for every temperature there is a certain constant relation between concentrations of CO and CO_2 in equilibrium with carbon.

In the system under consideration, thermodynamic reasoning leads to the conclusion that

$$\frac{[\text{CO}]^2}{[\text{CO}_2]} = \text{constant} = K,$$

in which [CO] and $[\text{CO}_2]$ denote the concentrations of CO and CO_2 , respectively, in gram molecules per liter.^d

^a See Meyer, O. E., *Kinetische Theorie der Gase*, 2d ed. (Breslau, 1899), sec. 101.

^b See Hoff, J. H. van't, *Chemical dynamics*, London, 1898, p. 228, and Haber, Fritz, *Thermodynamics of technical gas reactions*, p. 256.

^c The reverse arrows ($\rightleftharpoons$) used in place of the regular symbol ($=$) in the equation $\text{C} + \text{CO}_2 \rightleftharpoons 2\text{CO}$ denote that the reaction is reversible; that is, it may take place in the direction from left to right or from right to left.

^d A "gram molecule" of any substance is its molecular weight in grams; e. g., a gram molecule of H_2O is 18 grams, of CO, 28 grams, and of CO_2 , 44 grams.

Let $100x$ = percentage by volume of CO and $100(1-x)$ = percentage by volume of CO_2

Then
$$[\text{CO}] = x \frac{P}{R\theta}$$

$$[\text{CO}_2] = (1-x) \frac{P}{R\theta}$$

and
$$\frac{[\text{CO}]^2}{[\text{CO}_2]} = \frac{x^2}{(1-x)} \frac{P}{R\theta} = K.$$

Here R = the gas constant = $\frac{22.4}{273} = 0.0821$ liter atmospheres,

P = the pressure in atmospheres,

and θ = the absolute temperature.

$[\text{CO}]$ = the number of gram molecules of CO per liter.

$[\text{CO}_2]$ = the number of gram molecules of CO_2 per liter.

For constant conditions of pressure and temperature,

$$\frac{P}{R\theta} \text{ is a constant and } \frac{x^2}{1-x} = \text{constant} = K \frac{R\theta}{P}$$

The significance of this equation is that if a quantity of CO_2 gas is maintained in contact with carbon at constant temperature, θ , and pressure, P , the gas and the carbon will react rapidly at first, and then more and more slowly until the amount of CO formed is exactly $100x$ per cent of the total gas present.

THE REACTION-VELOCITY EQUATION.

Dynamic considerations as well as thermodynamic reasoning lead to the equation

$$\frac{[\text{CO}]^2}{[\text{CO}_2]} = K.$$

In the former case K takes the value $\frac{k_1}{k_2}$, where the k 's are the velocity coefficients of the two opposed reactions. The equation representing the rate of formation of CO by the reaction $\text{CO}_2 + \text{C} \rightleftharpoons 2\text{CO}$ may be written as follows:

$$\frac{d[\text{CO}]}{dt} = k_1[\text{CO}_2] - k_2[\text{CO}]^2. \quad (1)$$

When equilibrium is established

$$k_1[\text{CO}_2] = k_2[\text{CO}]^2$$

and

$$\frac{[\text{CO}]^2}{[\text{CO}_2]} = \frac{k_1}{k_2} = K.$$

If $100a$ = percentage of CO_2 by volume at time $t = 0$,

$100x$ = percentage of CO by volume at time t ;

and when

$$t = 0, x = 0,$$

then when

$$t = 0, \quad [\text{CO}_2] = a \frac{P}{R\theta} = M.$$

Let n = total number of CO molecules at time t , and m = total number of CO_2 molecules at time t .

Then if the initial volume is unity, $m = M - \frac{n}{2}$, and the corresponding volume at constant pressure is $1 + \frac{n}{2} \frac{R\theta}{P}$.

Then,

$$[\text{CO}] = x \frac{P}{R\theta} = \frac{n}{1 + \frac{n}{2} \frac{R\theta}{P}}$$

$$n = \frac{2x}{2-x} \frac{P}{R\theta}$$

and

$$[\text{CO}_2] = \frac{m}{1 + \frac{n}{2} \frac{R\theta}{P}} = \frac{M - \frac{n}{2}}{1 + \frac{n}{2} \frac{R\theta}{P}} = \frac{a \frac{P}{R\theta} - \frac{n}{2}}{1 + \frac{n}{2} \frac{R\theta}{P}} = \frac{a \frac{P}{R\theta} - \frac{x}{2-x} \frac{P}{R\theta}}{1 + \frac{x}{2-x} \frac{P}{R\theta}} = \frac{a - \frac{x}{2-x}}{1 + \frac{x}{2-x}} \frac{P}{R\theta}.$$

That is,

$$[\text{CO}_2] = \left(a - \frac{a+1}{2} x \right) \frac{P}{R\theta}$$

Introducing the values in equation (1) we obtain

$$\frac{dx}{dt} = k_1 \left(a - \frac{a+1}{2} x \right) - k_2 \frac{P}{R\theta} x^2,$$

and if

$$k'_2 = k_2 \frac{P}{R\theta}$$

$$\frac{dx}{dt} = k_1 \left(a - \frac{a+1}{2} x \right) - k'_2 x^2 \quad (2)$$

For the case that the initial gas is pure CO_2 , $a = 1$, and

$$\frac{dx}{dt} = k_1(1-x) - k'_2 x^2.$$

The integration of the differential equation (2) offers no great difficulty. The determination of the constants k_1 and k'_2 seems to have been made hitherto only by assuming the value of the ratio $\frac{k_1}{k'_2}$. This method is applicable when the equilibrium conditions are readily realized. As, however, this is not the case in the present reaction, it has been necessary to devise a method for the determination of k_1 and k_2 from any two or more pairs of simultaneous observation of x and t . It turns out that the method is applicable not only to the present reaction, but also to the general incomplete reaction of the second order.

The great difficulty of realizing, with certainty, the condition of the equilibrium in reactions like the one under consideration makes it highly desirable to obtain a general solution of the differential equation without introducing a particular numerical value of $\frac{k_1}{k'_2}$.

Prof. C. N. Haskins has obtained the solution of the differential equation (2) that is here presented.

1. Reduction and integration of the differential equation.

The differential equation is

$$\frac{dx}{dt} = k_1 \left(a - \frac{a+1}{2} x \right) - k'_2 x^2, \quad (2)$$

where

$$a = \frac{\text{per cent CO}_2}{100} \text{ at time } t=0,$$

$$x = \frac{\text{per cent CO}}{100} \text{ at time } t,$$

$$t = \text{time in seconds,}$$

and k_1 and k'_2 are the two constants of the reaction the values of which are sought. The initial condition is that

$$x=0, \text{ when } t=0.$$

To integrate, we introduce a new variable, z , and new constants, α and γ defined by the relations

$$\left. \begin{aligned} z &= \frac{x(a+1)}{4a-x(a+1)} & x &= \frac{4az}{(a+1)(z+1)} \\ \alpha &= \frac{1}{4} \sqrt{k_1^2(a+1)^2 + 16ak_1k'_2} & k_1 &= \frac{4\alpha\gamma}{a+1} \\ \gamma &= \sqrt{\frac{k_1(a+1)^2}{k_1(a+1)^2 + 16ak'_2}} & k'_2 &= \frac{\alpha(a+1)(1-\gamma^2)}{4a\gamma} \end{aligned} \right\} (3)$$

The differential equation becomes, under these substitutions

$$\frac{dz}{dt} = \frac{\alpha}{\gamma} (\gamma^2 - z^2) \quad (4)$$

with the initial conditions

$$z = 0, \text{ when } t = 0. \quad (5)$$

Integrating, we have

$$\ln^* \frac{\gamma + z}{\gamma - z} = 2\alpha t \quad (6)$$

and solving for z ,

$$z = \gamma \frac{e^{\alpha t} - e^{-\alpha t}}{e^{\alpha t} + e^{-\alpha t}} = \gamma \tanh \alpha t \quad (7)$$

whence, substituting in (3)

$$x = \frac{4a}{a+1} \frac{\gamma \tanh \alpha t}{1 + \gamma \tanh \alpha t}. \quad (8)$$

2. *The equation for γ and the criterion for the existence of one and only one root.*

We have (equation 8) an expression by means of which the percentage of CO at any time, t , may be computed if the constants γ and α are known. We now wish to determine γ and α from two pairs of observed corresponding values of t and x . Let these two pairs be $t_1 x_1$ and t_2, x_2 , and let $t_2 > t_1$. Then since a is known, we may compute

$$z_1 = \frac{x_1(a+1)}{4a - x_1(a+1)}, \quad z_2 = \frac{x_2(a+1)}{4a - x_2(a+1)}$$

and have

$$\ln \frac{\gamma + z_1}{\gamma - z_1} = 2 \alpha t_1, \quad \ln \frac{\gamma + z_2}{\gamma - z_2} = 2 \alpha t_2$$

from which γ and α are to be determined. Eliminating, α we readily obtain

$$\ln \frac{\gamma + z_2}{\gamma - z_2} = \frac{t_2}{t_1} \ln \frac{\gamma + z_1}{\gamma - z_1}. \quad (9)$$

The determination of γ and α depends therefore on the solution of this (transcendental) equation in γ . Consideration of the function

$$U(\gamma) \equiv t_1 \ln \frac{\gamma + z_2}{\gamma - z_2} - t_2 \ln \frac{\gamma + z_1}{\gamma - z_1}$$

and of its derivative

$$U'(\gamma) \equiv -2 \left(\frac{t_1 z_2}{\gamma^2 - z_2^2} - \frac{t_2 z_1}{\gamma^2 - z_1^2} \right)$$

* The symbols $\ln x$, $\log x$, will be used to denote the natural and the common logarithm of x , respectively.

shows that the equation

$$\ln \frac{\gamma + z_2}{\gamma - z_2} = \frac{t_2}{t_1} \ln \frac{\gamma + z_1}{\gamma - z_1} \quad (9)$$

has a root $\gamma > z_2$ when and only when

$$t_2 z_1 - t_1 z_2 > 0, \text{ that is, } \frac{z_2}{z_1} < \frac{t_2}{t_1} \quad (10)$$

If a root exists there is but one, and it satisfies the inequalities

$$z_2 < \gamma < \sqrt{z_1 z_2 \frac{(t_2 z_2 - t_1 z_1)}{t_2 z_1 - t_1 z_2}}.$$

The inequality (10) furnishes a negative criterion for the applicability of the differential equation (2) to a reaction under investigation. For if the reaction is governed by that equation, and if the observations are made with sufficient accuracy, there must exist a γ satisfying equation (9) and hence the inequality (10) must be satisfied. If then this inequality is not satisfied, and hence no such γ can be found, the assumptions involved in (2) must be invalid, or there must be error in the observations. On the other hand, if (10) is satisfied we can only conclude that (2) *may* be applicable, and we proceed to determine whether it is so by computing γ and α and comparing the values of x computed by means of (8) with the observed values of x .

3. Solution of the equation

$$\ln \frac{\gamma + z_2}{\gamma - z_2} = \frac{t_2}{t_1} \ln \frac{\gamma + z_1}{\gamma - z_1}.$$

If the selected pairs $t_1 x_1$, $t_2 x_2$ of observed values satisfy the criterion

$$\frac{z_2}{z_1} < \frac{t_2}{t_1} \quad (10)$$

we may compute γ in the equation as follows: Passing, for convenience of computation, from natural to common logarithms we have

$$\log \frac{\gamma + z_2}{\gamma - z_2} = \frac{t_2}{t_1} \log \frac{\gamma + z_1}{\gamma - z_1}.$$

Assume now a value for γ , say $\gamma = \gamma_v$ where

$$z_2 < \gamma < \sqrt{z_1 z_2 \frac{(t_2 z_2 - t_1 z_1)}{t_2 z_1 - t_1 z_2}}.$$

Then we may compute a quantity $\log N_1$ by the equation

$$\log N_1 = \frac{t_2}{t_1} \log \frac{\gamma + z_1}{\gamma - z_1}.$$

Determine now a new value of γ , $\gamma = \gamma_2$ by the relation

$$\log \frac{\gamma_2 + z_2}{\gamma_2 - z_2} = \log N_1$$

that is,

$$\frac{\gamma_2 + z_2}{\gamma_2 - z_2} = N_1$$

or ^a

$$\gamma_2 = \frac{N_1 + 1}{N_1 - 1} z_2.$$

Proceed now to determine a new approximation γ_3 from γ_2 in the same way that γ_2 was determined from γ_1 and continue the process until its repetition produces no change, or a change which is negligible compared with the experimental errors. It will be found that in general the process converges somewhat rapidly, and only a few repetitions are necessary.

Suppose, then, that γ has been found by this process. Then α is computed by either of the relations

$$2\alpha = \frac{1}{t_1} \ln \frac{\gamma + z_1}{\gamma - z_1}, \quad 2\alpha = \frac{1}{t_2} \ln \frac{\gamma + z_2}{\gamma - z_2}$$

or, what amounts to the same thing, if N is the last of the numbers $N_1, N_2, \dots$ used in computing γ

$$2\alpha = \frac{1}{t_2} \ln \frac{\gamma + z_2}{\gamma - z_2} = \frac{1}{t_2} \ln N = \frac{1}{t_2} \log N \ln 10$$

$$2\alpha = \frac{2.3026}{t_2} \log N.$$

4. Computation of reaction constants k_1 , k'_2 , and verification of reaction equation.

When the constants α , γ have been computed we can find the original constants k_1 , k'_2 by the relations

$$k_1 = \frac{4\alpha\gamma}{a+1}$$

$$k'_2 = \frac{\alpha(a+1)(1-\gamma^2)}{4a\gamma} \quad (3)$$

To determine the applicability of the reaction equation (2) to the case in hand we have now only to introduce the values just found into the equation

$$z = \gamma \tanh \alpha t \quad (7)$$

or

$$x = \frac{4a}{a+1} \frac{\gamma \tanh \alpha t}{1 + \gamma \tanh \alpha t} \quad (8)$$

^a This computation may be abridged by the use of Gaussian logarithms.

and compare the values of z or x given with those found by observation. For this purpose equation (7) is the simpler, especially when the z 's corresponding to observed values of x have been already computed.

5. *Correction of constants α and γ by the method of least squares.*

The constants α , γ obtained above are determined by two pairs of observations only. It is, of course, desirable that all the observations be used in fixing their values, as on account of experimental errors the values obtained from different pairs of observations will in general not be identical. We proceed, therefore, to correct the constants by the method of least squares.

Let $t_1, x_1; t_2, x_2; \dots t_n, x_n$, be the n observed pairs of values of t and x . The problem is, then, to determine α and γ in such a way that if

$$\ln \frac{\gamma + z_i}{\gamma - z_i} - 2\alpha t_i \equiv \delta_i$$

then

$$n\delta^2 \equiv \sum_1^n i\delta_i^2,$$

shall be a minimum.

In order that α and γ shall make $n\delta^2$ a minimum they must satisfy the so-called normal equations.

$$\frac{n}{2} \frac{d\delta^2}{d\alpha} \equiv \sum_1^n i\delta_i \frac{d\delta_i}{d\alpha} \equiv \sum_1^n i2t_i \left\{ 2\alpha t_i - \ln \frac{\gamma + z_i}{\gamma - z_i} \right\} = 0,$$

$$\frac{n}{2} \frac{d\delta^2}{d\gamma} \equiv \sum_1^n i\delta_i \frac{d\delta_i}{d\gamma} \equiv \sum_1^n i \left\{ \frac{1}{\gamma + z_i} - \frac{1}{\gamma - z_i} \right\} \left\{ \ln \frac{\gamma + z_i}{\gamma - z_i} - 2\alpha t_i \right\} = 0$$

These equations may be written

$$2\alpha \sum_1^n i t_i^2 + \sum_1^n i t_i \ln \frac{\gamma - z_i}{\gamma + z_i} = 0.$$

$$2\alpha \sum_1^n i \frac{t_i z_i}{\gamma^2 - z_i^2} + \sum_1^n i \frac{z_i}{\gamma^2 - z_i^2} \ln \frac{\gamma - z_i}{\gamma + z_i} = 0$$

As their exact solution in their present form is impracticable on account of their complexity, we replace them in the usual way by a system of approximately equivalent lineal equations, by making use of the fact that the quantities u , v by which α and γ differ from α_0 and γ_0 respectively are small compared with α_0 , γ_0 .

Substituting

$$\alpha = \alpha_0 + u$$

$$\gamma = \gamma_0 + v$$

we have

$$\begin{aligned} 2u \sum_1^n i t_i^2 + \sum_1^n i t_i \ln \left(\frac{1 + \frac{v}{\gamma_0 - z_i}}{1 + \frac{v}{\gamma_0 + z_i}} \right) &= \sum_1^n i t_i \left\{ \ln \frac{\gamma_0 + z_i}{\gamma_0 - z_i} - 2\alpha_0 t_i \right\} \\ 2u \sum_1^n i \frac{t_i z_i}{(\gamma_0^2 - z_i^2)} + \sum_1^n i \frac{z_i \ln \left(\frac{1 + \frac{v}{\gamma_0 - z_i}}{1 + \frac{v}{\gamma_0 + z_i}} \right)}{(\gamma_0^2 - z_i^2)} &= \sum_1^n i \frac{z_i \left\{ \ln \left(\frac{\gamma_0 + z_i}{\gamma_0 - z_i} \right) - 2\alpha_0 t_i \right\}}{(\gamma_0^2 - z_i^2) \left(1 + \frac{2\gamma_0 v + v^2}{\gamma_0^2 - z_i^2} \right)} \\ &= \sum_1^n i \frac{z_i \left\{ \ln \left(\frac{\gamma_0 + z_i}{\gamma_0 - z_i} \right) - 2\alpha_0 t_i \right\}}{(\gamma_0^2 - z_i^2) \left(1 + \frac{2\gamma_0 v + v^2}{\gamma_0^2 - z_i^2} \right)} \end{aligned}$$

Expanding the logarithms by Maclaurin's series and neglecting terms of the order of uv and v^2 in comparison with those of the order of u and v we have

$$\begin{aligned} u \sum_1^n i t_i^2 + v \sum_1^n i \frac{t_i z_i}{\gamma_0^2 - z_i^2} &= \sum_1^n i t_i \left(\ln \frac{\gamma_0 + z_i}{\gamma_0 - z_i} - 2\alpha_0 t_i \right) \\ u \sum_1^n i \frac{t_i z_i}{\gamma_0^2 - z_i^2} + v \sum_1^n i \frac{z_i^2}{(\gamma_0^2 - z_i^2)^2} &= \sum_1^n i \frac{z_i}{(\gamma_0^2 - z_i^2)} \left(\ln \frac{\gamma_0 + z_i}{\gamma_0 - z_i} - 2\alpha_0 t_i \right) \end{aligned}$$

Expressing the natural logarithms in terms of common logarithms we have, putting

$$A_i \equiv t_i, \quad B_i \equiv \frac{z_i}{\gamma_0^2 - z_i^2}, \quad C_i \equiv \log \frac{\gamma_0 + z_i}{\gamma_0 - z_i} - M t_i,$$

$$K = \frac{\ln 10}{2} = 1.15129, \quad M = \frac{2\alpha_0}{\ln 10} = 0.86589\alpha_0:$$

$$u \sum_1^n i A_i^2 + v \sum_1^n i A_i B_i = K \sum_1^n i A_i C_i$$

$$u \sum_1^n i B_i A_i + v \sum_1^n i B_i^2 = K \sum_1^n i B_i C_i$$

or in the usual notation of the method of least squares

$$u[AA] + v[AB] = K[AC]$$

$$u[BA] + v[BB] = K[BC]$$

From these equations u and v are readily computed, and hence the corrected values

$$\alpha = \alpha_0 + u$$

$$\gamma = \gamma_0 + v$$

are found.

6. *Application of the method of solution to other equations of reaction velocity.*

The well-known equation^a

$$\frac{dx}{dt} = k_1(1-x)^2 - k_2 x^2:$$

with the initial conditions

$$x=0 \text{ when } t=0$$

is reducible by the substitutions

$$\begin{array}{ll} z = \frac{x}{1-x} & x = \frac{z}{1+z} \\ \alpha = \sqrt{k_1 k_2} & k_1 = \alpha \gamma \\ \gamma = \sqrt{\frac{k_1}{k_2}} & k_2 = \frac{\alpha}{\gamma} \end{array}$$

to the form we have considered, viz:

$$\frac{dz}{dt} = \frac{\alpha}{\gamma}(\gamma^2 - z^2) \quad (4)$$

with the initial conditions $z=0$ when $t=0$ its integral is, therefore,

$$\ln \frac{\gamma+z}{\gamma-z} = 2\alpha t \quad (6)$$

or

$$z = \gamma \tanh \alpha t \quad (7)$$

or

$$x = \frac{\gamma \tanh \alpha t}{1 + \gamma \tanh \alpha t} \quad (8)$$

^a Nernst, Walther, Theoretische Chemie, 5th edition, p. 564; 2d English edition, p. 568.

and the constants are determined by the equation

$$\ln \frac{\gamma + z_2}{\gamma - z_2} = \frac{t_2}{t_1} \ln \frac{\gamma + z_1}{\gamma - z_1} \quad (9)$$

if the criterion

$$\frac{z_2}{z_1} < \frac{t_2}{t_1} \quad (10)$$

is satisfied.

The more general equation ^a

$$\frac{dx}{dt} = k_1(a_1 - x)(b_1 - x) - k_2(a_2 + x)(b_2 + x)$$

with initial conditions $x=0$ when $t=0$, is reducible by a substitution of the form

$$x = \frac{\rho z - \sigma}{1 + z}$$

where ρ and σ are constants depending on a_1, b_1, a_2, b_2 , but not on k_1, k_2 , to the equation

$$\frac{dz}{dt} = \frac{\alpha}{\gamma} (\gamma^2 - z^2) \quad (4)$$

The initial conditions, however, are now not

$$t=0, \quad z=0 \quad (5)$$

but

$$t=0, \quad z = \frac{\sigma}{\rho} \equiv z_0$$

and hence the integral and the equation determining the constants are more complex.

The equation determining γ is

$$\ln \frac{\gamma + z_2}{\gamma - z_2} = \frac{t_2}{t_1} \ln \frac{\gamma + z_1}{\gamma - z_1} - \left[\left(\frac{t_2}{t_1} - 1 \right) \ln \frac{\gamma + z_0}{\gamma - z_0} \right]$$

and the criterion for the existence of a solution is

$$t_2 z_1 - t_1 z_2 - (t_2 - t_1) z_0 > 0$$

7. Calculation of x .

Using the data given in Tables 1 and 2 (pp. 11, 14), the values of γ and α , and hence of k_1, k_2 , and K , have been calculated by the method of least squares as described above. The constants for charcoal are tabulated in Table 4.

^a Nernst, Walther, Theoretische Chemie, 5th edition, p. 543; 2d English edition, p. 542.

The last column of each of Tables 1 to 3 contains values of x calculated from the equation

$$x = \frac{4a}{a+1} \frac{\gamma \tanh \alpha t}{1 + \gamma \tanh \alpha t}. \quad (8)$$

The CO_2 used was nearly pure, and therefore $a=1$, whence,

$$x = \frac{2\gamma \tanh \alpha t}{1 + \gamma \tanh \alpha t}$$

The calculated and observed values of x agree within 2 or 3 per cent.

TABLE 4.—*Constants used in computation of x (charcoal).*

Temperature (°C.).	a ($a=1$)	γ ($a=1$)	k'_2	k_2	k_1	$K = \frac{k_1}{k_2}$
800	0.0276	0.3568	0.03373	3.031	0.01968	0.006493
850	0.0612	0.5853	0.03443	3.238	0.07174	0.02216
900	0.09998	0.7711	0.02646	2.599	0.1540	0.05925
925	0.1297	0.8388	0.02291	2.298	0.2175	0.09465
1,000	0.3617	0.8853	0.04416	4.708	0.6404	0.1360
1,100	0.7921	0.9437	0.04588	5.275	1.495	0.2834

The curves in figures 3, 4, 5, and 6 were plotted from values of x (per cent CO) calculated from equation (8). The observed values are indicated by the small circles. By means of equation (8) it is possible to calculate the percentage of CO corresponding to any given gas velocity, providing α and γ or k_1 and k_2 are known. The values of k_1 and K , as well as α and γ , given in Table 4, exhibit a systematic variation with temperature. If an equation can be found which will express k_1 and K as a function of temperature, it will then be possible to calculate the percentage of CO for any time of contact and any desired temperature.

8. Variations of K and k_1 with temperature.

By thermodynamical considerations Van't Hoff has derived the following expressions for the variation of the constant of equilibrium, K , and the coefficient of reaction velocity, k , with temperature.

$$\frac{d(\ln K)}{d\theta} = -\frac{Q}{R\theta^2}$$

and

$$\frac{d(\ln k)}{d\theta} = \frac{A}{\theta^2} + B.$$

In these equations Q is the latent heat of reaction at the absolute temperature θ ; A is a function of Q , but is selected arbitrarily. B is

an arbitrary function of the temperature. By integration the latter equation becomes

$$\ln k = -\frac{A}{\theta} + B\theta + C, \quad 11$$

where C is an integration constant. The values of A , B , and C in equation (11) have been determined from the simultaneous values of k_1 and θ of Table 1. Table 5 contains the values of k_1 observed at various temperatures, k_1 (obs.), as well as the values of k_1 calculated from equation (11), k_1 (cal.). The agreement is remarkably good, showing that the velocity coefficient, k_1 , follows the differential equation which holds for most rates or reactions.

TABLE 5.—Variation of k_1 with temperature (charcoal).

$$[\ln k_1 = -\frac{50910}{\theta} - 0.0203 \theta + 65.376]$$

Temperature (°C).	θ	k_1 (obs.).	k_1 (cal.).
800	1.073	0.020	0.021
850	1.123	0.073	0.064
900	1.173	0.154	0.159
925	1.198	0.217	0.237
1,000	1.273	0.640	0.629
1,100	1.373	1.49	1.53

In order to integrate the equation

$$\frac{d(\ln K)}{d\theta} = -\frac{Q}{R\theta^2}$$

it is first necessary to determine Q as a function of temperature. Kirchoff has shown that the increment of Q per degree centigrade is equal to the difference of the molecular heats of the factors and of the products of the reaction:

$$Q = Q_0 + (\sigma_{\text{CO}_2} + \sigma_{\text{C}} - 2\sigma_{\text{CO}})\theta$$

Q_0 = The heat of reaction at $\theta = 0$.

σ = molecular heat at temperature θ .

σ_0 = molecular heat at temperature $\theta = 0$.

$$\sigma' = \frac{1}{2} \frac{d\sigma}{d\theta}$$

Assuming that σ is a linear function of temperature, which is very nearly true for gases

$$Q = Q_0 + \Sigma(\sigma_0)\theta + \Sigma(\sigma')\theta^2$$

$$\frac{d(\ln K)}{d\theta} = -\frac{1}{R} \left[\frac{Q_0}{\theta^2} + \frac{\Sigma(\sigma_0)}{\theta} + \Sigma(\sigma') \right]$$

$$\ln K = \frac{1}{R} \left[\frac{Q_0}{\theta} - \Sigma(\sigma_0) \ln \theta - \Sigma(\sigma')\theta + C \right] \quad (1)$$

The constants in this equation (12) may be evaluated by two different methods: by experimental determinations of Q , σ_0 , and σ' , or from four or more simultaneous observations of K and θ . The first method was adopted in this instance. The third column of Table 6 contains the values of K calculated by means of equation (12), taking

$$Q_0 = -40166$$

$$\Sigma(\sigma_0) = -2.055$$

$$\Sigma(\sigma') = .003104$$

$$C = 8.604$$

The values in the column marked K (obs.) are the constants obtained from the observed values of x and T in Table 1.

TABLE 6.—*Values of K from experimental determinations.*

$$[\ln K = -\frac{20235}{\theta} + 1.0357 \ln \theta - 0.001564\theta + 8.604]$$

Temperature (°C).	K (obs.).	K (cal.).	x_∞ (obs.).	x_∞ (cal.).	x_∞ (obs.) Boudouard.
500		0.000007		0.021	
600		0.00013		0.093	
650		0.00046		0.185	0.39
700		0.00137		0.283	
800	0.0065	0.0090	0.526	0.582	0.93
850	0.022	0.020	0.738	0.722	
900	0.059	0.042	0.871	0.832	
925	0.094	0.060	0.912	0.873	0.96
1,000	0.136	0.151	0.939	0.945	
1,100	0.283	0.448	0.971	0.981	
1,200		1.120		0.944	
1,300		2.455		0.997	
1,400		4.826		0.9985	
1,500		8.671		0.9992	
1,600		14.44		0.9996	

In the fourth column of Table 6 are the observed values of x_∞ , the amount of CO in equilibrium with CO₂ and charcoal at temperatures from 800° to 1,100° C., and in the fifth column the values of x corresponding to the values of K in the third column. For the specific heats of CO and CO₂, Langen's values were used, and for the specific heat of charcoal, Kunz's. Q_0 was calculated from the heats of combustion of carbon (amorphous) and carbon monoxide at ordinary temperatures.^a C was calculated from equation (12) using all the values of K (obs.) by the method of least squares.

The constants of equation (12) were calculated also by the method of least squares from simultaneous values of K (obs.) and θ , but the agreement was less satisfactory than in the former method.

The agreement between observed and calculated values of K and k_1 in Tables 5 and 6 shows that the increase of K or k_1 with temperature

^a Ostwald, W., *Grundriss der Allgemeinen Chem.*, 3d ed., p. 267.

follows Van't Hoff's laws. It is possible, therefore, by means of equations (11) and (12) and the values of the constants of these equations given in Tables 5 and 6 to compute K and k_1 for any desired temperature. For any temperature for which K and k_1 , and consequently k_2 ($k_2 = \frac{k_1}{K}$), have been computed, x , the per cent of CO corresponding to any time of contact, t , can then be calculated by means of equation (8).

TABLE 7.—Variation of x_∞ (per cent CO in equilibrium with CO_2 and C) with temperature.

Temperature (°C.).	x_∞ (cal.)	x_∞ (obs.) Charcoal.	x_∞ (obs.) Coke.	x_∞ (obs.) Anthracite.
900	0.832	0.871	0.875	
1,000	0.945	0.939	0.886	
1,100	0.981	0.971	0.968	0.914
1,200	0.994		0.987	0.994
1,300	0.997		0.996	0.997

TABLE 8.—Variation of k_1 with temperature (coke).

$$[\ln k_1 = -\frac{47220}{\theta} - 0.009699\theta + 45.597.]$$

Temperature (°C.).	θ	k_1 (obs.).	k_1 (cal.).
900	1,173	0.0024	0.0023
1,000	1,273	0.021	0.023
1,100	1,373	0.121	0.134
1,200	1,473	0.473	0.410
1,300	1,573	1.38	1.48

TABLE 9.—Variation of k_1 with temperature (anthracite).

$$[\ln k_1 = \frac{31972}{\theta} + 0.02272\theta - 56.607.]$$

Temperature (°C.).	θ	k_1
1,100	1,373	0.119
1,200	1,473	0.237
1,300	1,573	0.579

The percentages of CO in equilibrium with CO_2 and charcoal, coke, and anthracite, respectively, x , are given in Table 7. The values of x in the second column of this table were calculated from the values of K in the third column of Table 6 by means of the equation

$$\frac{x^2}{1-x} = K \frac{R\theta}{P}$$

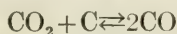
A comparison of figures 3, 5, and 6 shows that the reaction velocity is greatest with charcoal and lowest with anthracite. The tempera-

ture coefficient of k_1 was determined for anthracite and coke in the same manner as for charcoal. The observed and calculated values of k_1 are shown in Tables 8 and 9.

The constant, k_2 in the equation

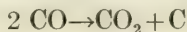
$$\frac{d(\text{CO})}{dt} = k_1(\text{CO}_2) - k_2(\text{CO})^2$$

is the coefficient of reaction velocity of the reaction



in the direction from right to left. At the temperatures of these experiments, $800^\circ - 1,300^\circ \text{C}$, the carbon produced by the decomposition of CO is in the form of lampblack, regardless of the form of carbon present in the reaction tube—charcoal, coke, or coal. At any one temperature, therefore, k_2 should be the same in all three cases. From a comparison of Tables 1 to 3 it will be seen that there is considerable deviation in the values of k_2 for the three forms of carbon used. This is doubtless due in part to experimental errors. There is a further consideration, however, to which attention should be called, viz, that the reaction in question is not strictly reversible.

The lampblack produced by the reverse reaction



is not identical, physically, with the form of carbon, charcoal, or coke, which is consumed in the formation of CO. Consequently, the law of chemical mass action is not strictly applicable. In the system under consideration, equilibrium would not be reached until all the carbon has been transformed to lampblack.

DISCUSSION AND CONCLUSIONS.

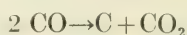
RESULTS OF BOUDOUARD'S INVESTIGATIONS.

The results of Boudouard's investigations of the percentage of CO in equilibrium with CO_2 and carbon, referred to on pages 6 and 7, are also given in the last column of Table 6. A comparison of Boudouard's values with those obtained in our experiments shows a decided disagreement, Boudouard's values for CO being higher in every case. The writers are unable to account for so great a discrepancy. It is to be noted, however, that in the analysis of his gases Boudouard apparently determined CO_2 directly and CO by differences, so that any air which might have been present in the gases would have been reported as CO.

It does not seem likely that errors in the measurement of temperature could be responsible for differences of so great a magnitude in the amount of CO formed.

As stated on page 9, and illustrated in figure 1, in all the experiments the hot junction of the thermocouple was imbedded in the carbon within the reaction tube, and the couple was calibrated at frequent intervals. Also, the cold junction was maintained at 0°C . The error in the temperature measurements could not exceed 15° or 20°C . Moving the couple through the portion of the tube occupied by carbon showed that there were no temperature differences in the carbon bed greater than 10°C . It is not apparent from Boudouard's account of his experiments what precautions were observed to insure accurate temperature measurements.

That the percentage of CO obtained in the writer's experiments was not reduced appreciably by the reverse reaction



taking place during the passage of the gases through the region of falling temperature at the exit end of the tube is indicated by the fact that no deposit of carbon could be observed at this portion of the tube.

REACTION KINETICS.

Van't Hoff has shown that the coefficient of reaction velocity, k , for a number of reactions increases between 2 and 2.5 fold for a rise of temperature of 10°C .

The reactions considered by Van't Hoff were investigated at temperatures below 100°C . At higher temperatures the rate of increase in k with rise of temperature is lower.

If for a given reaction, at a temperature of 100°C .

$$\frac{k_{\theta+10}}{k_{\theta}} = 2.5,$$

it follows from Van't Hoff's equation,

$$\frac{d(\ln k)}{d\theta} = \frac{A}{\theta^2},$$

that for $T=1,000^{\circ}$, $\theta=1,273^{\circ}$,

$$\frac{k_{\theta+10}}{k_{\theta}} = 1.08.$$

In table 10 the values of the ratio $\frac{k_{\theta+10}}{k_{\theta}}$ corresponding to the results in Tables 5, 8, and 9 indicate that the increase of k with rise in temperature is of the magnitude which might be expected for reaction velocities in homogeneous systems.

TABLE 10.—Increase in k with a rise in temperature of 10° C.

Form of carbon.	Temperature range ($^\circ$ C.).	$\frac{k_{\theta+10}}{k_{\theta}}$
Charcoal.....	800-1,100	1.155
Coke.....	900-1,300	1.175
Anthracite.....	1,100-1,300	1.082

It has been previously stated (p. 20) that the speed of chemical reactions increases far more rapidly with rise of temperature than the rate of diffusion of gases.

Table 11 gives the observed increase in velocity of the reaction $\text{CO}_2 + \text{C} = 2\text{CO}$, and the increase in rate of diffusion over the same temperature intervals calculated on the assumption that diffusion increases with the square of the temperature.

TABLE 11.—Relative rates of increase in reaction velocity and diffusion constant.

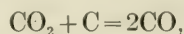
Form of carbon.	Temperature range ($^\circ$ C.).	Observed increase in reaction velocity (k_1).	Calculated increase in diffusion constant.
Charcoal.....	800-1,100	75 fold	1.64 fold
Coke.....	900-1,300	576 fold	1.80 fold
Anthracite.....	1,100-1,300	4.9 fold	1.31 fold

It seems probable from the high values of the increase of k_1 with rising temperature, found in our experiments and shown in the third column of this table, that the determining factor in speeds of the reactions under consideration is the velocity of chemical combination and not of diffusion.

But aside from the question as to whether or not the laws of reaction velocity apply to the heterogeneous reaction, $\text{CO}_2 + \text{C} = 2\text{CO}$, the equations given in this paper expressing x as a function of t , and k_1 and K as functions of the temperature, fit the experimental results obtained. These equations, therefore, furnish a means for calculating the percentage of CO formed for any value of t , the time of contact, and T , the temperature at which the reaction takes place.

SUMMARY.

1. The rate of formation of CO in the reaction



has been determined, with charcoal from 800° to $1,100^\circ$ C., with coke from 900° to $1,300^\circ$ C., and with anthracite from $1,100^\circ$ to $1,300^\circ$ C.

2. The differential equation for the velocity of the incomplete reaction, $\text{CO}_2 + \text{C} \rightleftharpoons 2\text{CO}$,

$$\frac{dx}{dt} = k_1 \left(a - \frac{a+1}{2}x \right) - k'_2 x^2$$

has been solved for k'_2 and k_1 , and it has been shown that the method is applicable to other cases.

3. Van't Hoff's laws for the variation of equilibrium constants and coefficients of reaction velocity with temperature have been applied to the values of k_1 and K obtained in these experiments and a close agreement found between observed and calculated values.

4. From a consideration of the temperature coefficients of k_1 , it is probable that velocity of chemical combination and not diffusion is the determining factor in the speed of the reaction.

5. By means of the equations expressing the laws referred to in paragraphs 2 and 3, it is possible to compute the percentage of CO, which is formed at any temperature and with any time of contact.

6. It has been shown that, for the production of a high percentage of CO, the producer fuel bed should have a temperature of $1,300^\circ \text{C}$. or over, and that increasing the depth of the hot portion of the bed will increase the percentage of CO generated and consequently the capacity of the producer, at first rapidly and then more and more slowly.

7. To minimize the production of CO in the boiler furnace the fuel bed should be thin. Increasing the velocity of the gas will tend to decrease rather than increase the percentage of CO formed.

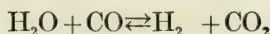
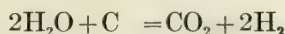
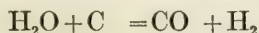
EFFECTIVE TEMPERATURES FOR WATER-GAS GENERATION.

By J. K. CLEMENT and L. H. ADAMS.

INTRODUCTION.

The object of this paper is to describe investigations which were carried on in the physical laboratory of the technologic branch of the United States Geological Survey to determine the influence of temperature on the rate of formation and on the composition of water gas, and to ascertain the most favorable conditions for the economical production of combustible gases from water vapor and carbon.

Incandescent carbon combines readily with water vapor, forming a mixture of hydrogen, carbon monoxide, carbon dioxide, and, as is shown by the results of the investigation described, a small quantity of methane. The principal reactions are represented by the equations



The composition of the gas obtained when a stream of superheated steam is passed through a bed of glowing carbon, as well as the quantity of steam decomposed in a given time, vary with the temperature, the rate of flow, and the kind of carbon used.

DESCRIPTION OF EXPERIMENTS.

APPARATUS AND METHODS.

The methods employed were substantially the same as had been used in the preceding investigation of the reactions between carbon dioxide and carbon (pp. 9, 10). Carbon—coke or charcoal—crushed and screened to pieces about 5 mm. in diameter was placed in a tube of refractory material (Berlin porcelain or quartz glass) and a current of superheated steam passed through it.

Heating coil and superheater.—The arrangement of apparatus is illustrated in figure 8. Steam was generated by means of an electric heating coil and passed through a spiral copper-tube superheater, and thence into the top of the reaction tube. By regulating the

current in the heating coil, the rate of flow of steam could be readily adjusted to any desired value, and its flow made uniform.

Electric furnace and reaction tube.—The electric furnace shown in figure 8 is of the same general type as that used in the experiments with carbon dioxide and carbon already described. The nickel heating coil of the earlier furnace, however, was replaced by one of "nichrome" wire obtained from the Driver-Harris Company, of Harrison, N. J. Compared with nickel, this alloy possesses the advantages of lower temperature coefficient of resistance, higher fusion point, and less tendency to become brittle at high temperatures.

A number of experiments were made with the furnace at a temperature of $1,300^{\circ}\text{C.}$, and it is not improbable that a somewhat higher temperature may be produced without destroying the heating coil.

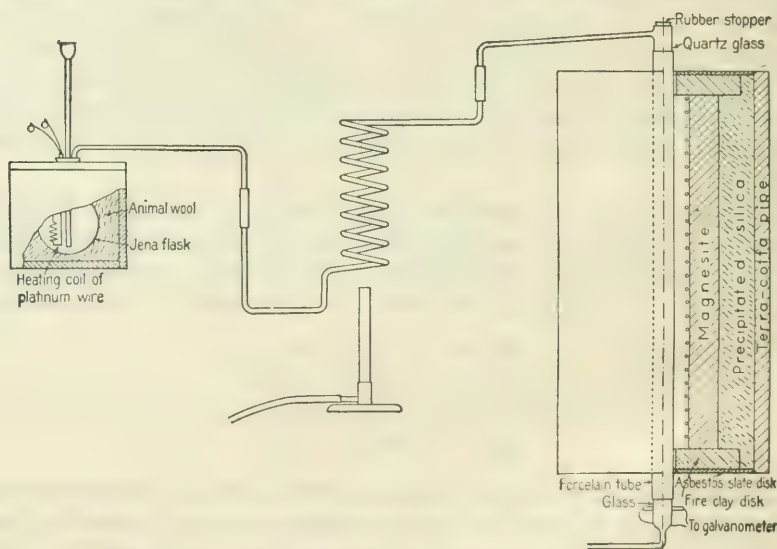


FIGURE 8.—Arrangement of heating coil, superheater and electric furnace

Figure 8 shows the reaction tube in position in the furnace. By means of suitable rheostats any temperature up to $1,300^{\circ}\text{C.}$ could be readily obtained, and the temperature could be kept constant to within 1° or 2°C.

In order to have the temperature of the reacting material as nearly uniform as possible, only the central portion of the tube was filled with carbon. The lower part of the tube was filled with pieces of broken porcelain, which, in addition to forming a support for the carbon, reduced the size of the passageway, thereby increasing the velocity of the gas, through the region of variable temperature.

After three weeks' use at 800° and 900°C. —the furnace being allowed to cool at night during the first two weeks and being heated continuously during the third week—the quartz-glass tube was found to be completely devitrified. All experiments at $1,000^{\circ}\text{C.}$ and over and four experiments at 900°C. were made in a tube of Berlin porcelain.

Analysis of gases.—After passing through the reaction tube the gas was led in turn through an empty U-shaped drying tube and a tube containing calcium chloride, in which the moisture was condensed and weighed. The fixed gases were then collected over mercury and analyzed, in Babb's improved Orsat apparatus, for CO_2 , O_2 , CO , H_2 , and CH_4 . The analyses were checked from time to time by the Hempel method.

Measurement of temperatures.—Temperature measurements were made by means of a platinum-rhodium thermocouple and a high resistance millivoltmeter. At the higher temperatures the thermocouple wires deteriorated rapidly—probably because of the reducing action of the gases on the insulating tubes or on the ash of the coke—and the hot portion of the wires became brittle and fell to pieces. The couple had to be frequently repaired by removing the contaminated part and re-fusing the wires, and finally had to be replaced by a new couple.

TABLE 12.—Results of experiments with coke at 800° to 1,300° C.

No. of experiment.	Temperature (°C.).	Time of contact in seconds, <i>t</i> .	$\frac{1}{t}$	Composition of dry gas (per cent.).					Composition of total gas (per cent.).				
				CO_2 .	CO .	H_2 .	CH_4 .	Total.	H_2O .	CO_2 .	CO .	H_2 .	CH_4 .
1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	800	1.019	0.983	4.8	34.4	42.5		81.7	99.1	0.06	0.40	0.49	
2	800	.627	1.594	3.6	31.3	41.7		76.6	99.4	.03	.25	.34	
3	800	.416	2.40	4.2	35.0	45.5		84.7	99.6	.02	.16	.21	
4	900	8.35	.120	9.8	30.4	45.7	2.0	87.9	75.4	2.75	8.51	12.78	0.57
5	900	2.96	.337	6.8	39.8	47.5	1.9	96.0	89.5	.75	4.36	5.22	.21
6	900	2.88	.347	8.1	37.0	46.7	2.1	93.9	89.5	.91	4.16	5.25	.23
7	900	1.47	.679	7.9	36.0	46.6	1.8	92.3	92.9	.61	2.78	3.60	.14
8	900	1.37	.728	6.0	41.2	47.8	1.7	96.7	92.3	.48	3.29	3.82	.14
9	900	.721	1.387	6.4	40.1	47.9	2.2	96.6	95.0	.33	2.08	2.50	.11
10	900	.608	1.643	4.8	41.3	47.9	1.6	95.6	95.6	.27	2.34	2.71	.08
11	900	.500	2.000	6.0	40.8	47.5	1.9	96.2	96.2	.24	1.62	1.88	.08
12	900	.442	2.262	5.5	42.7	48.1	1.6	97.9	96.7	.19	1.45	1.63	.05
13	900	.428	2.336	5.4	41.3	47.4	1.8	95.9	97.4	.15	1.12	1.28	.05
14	900	.272	3.68	4.9	41.9	51.8		98.6	98.0	.10	.86	1.06	
15	900	.245	4.08	5.9	39.5	48.0	1.2	94.6	97.9	.13	.90	1.09	.03
16	1,000	6.98	.142	13.6	28.6	49.3	2.6	94.1	69.8	4.38	9.16	15.80	.84
17	1,000	3.42	.292	10.7	33.6	50.3	2.0	96.6	78.4	2.40	7.53	11.28	.45
18	1,000	2.64	.379	9.6	35.1	48.4	1.9	95.0	81.3	1.89	6.92	9.56	.37
19	1,000	1.504	.666	8.7	37.3	49.7	1.9	97.6	84.2	1.41	6.05	8.07	.30
20	1,000	1.025	.976	7.8	38.0	48.5	1.6	95.9	88.7	.91	4.48	5.71	.19
21	1,000	.733	1.364	7.2	38.6	48.7	1.7	96.2	90.6	.70	3.76	4.75	.17
22	1,000	.437	2.29	8.0	38.2	49.3	1.8	97.3	93.7	.52	2.48	3.22	.11
23	1,000	.244	4.08	7.1	39.0	48.1	1.9	96.1	96.4	.27	1.47	1.81	.08
24	1,100	7.97	.1255	14.6	28.1	53.1	1.4	97.2	34.9	9.8	18.8	35.6	.90
25	1,100	1.970	.507	12.8	28.9	51.2	1.5	94.4	67.6	4.40	9.92	17.6	.51
26	1,100	1.034	.967	13.3	30.5	52.5	1.9	98.2	76.8	3.16	7.22	12.41	.44
27	1,100	.493	2.026	14.8	28.0	54.1	1.4	98.3	88.6	1.73	3.25	6.30	.16
28	1,100	.377	2.65	13.4	28.9	51.5	1.7	95.5	90.1	1.39	3.00	5.36	.18
29	1,100	.259	3.85	13.3	30.4	53.1	1.4	98.2	92.0	1.09	2.48	4.32	.11
30	1,200	11.05	.0903	.3	51.8	42.9	1.0	96.0	5.0	.3	51.3	42.5	1.0
31	1,200	4.48	.2224	.6	52.1	43.1	1.2	97.0	17.0	.5	44.6	37.0	.9
32	1,200	2.132	.468	.9	48.6	44.8	1.5	95.8	52.3	.4	24.2	22.3	.8
33	1,200	.866	1.155	7.4	39.3	49.4	1.2	97.3	74.8	1.92	10.18	12.80	.31
34	1,200	.478	2.084	11.5	33.1	53.4	1.1	99.1	80.8	2.23	6.43	10.37	.23
35	1,200	.337	2.96	3.6	46.3	47.0	1.9	98.8	83.0	.62	8.00	8.11	.32
36	1,300	4.32	.2314	.4	50.5	43.7	1.9	96.5	.0	.4	52.4	45.3	2.0
37	1,300	2.25	.443	.3	49.2	42.4	1.7	93.6	2.1	.3	51.5	44.3	1.8
38	1,300	1.633	.612	.3	49.5	43.9	1.8	95.5	7.7	.3	47.8	42.5	1.7
39	1,300	1.245	.802	.3	49.5	45.8	1.9	97.6	17.4	.3	41.9	38.8	1.6

The measurements of temperatures were accurate within about 5° below 1,100° C. and within 5° to 15° between 1,100° and 1,300° C.

RESULTS OF EXPERIMENTS.

EXPERIMENTS WITH COKE.

The results of the experiments with coke are given in Table 12. The time of contact, t , given in column 3, was calculated from the equation $t = S \frac{v \theta_r}{V \theta}$ where S is the time required to fill sample tube, θ and θ_r the absolute temperature of the carbon and of the sample tube, respectively, V the volume of the sample tube, and v the volume of the free passages through the carbon. The latter is determined by the dimensions of the portion of the reaction tube which is occupied by carbon and the weight and apparent density of the carbon. Since v can not be determined accurately and the formula for t rests on the assumption that the volume of the gas undergoes no change during the reaction, t is only approximately correct. The errors in t , however, are nearly constant, so that the values given in the table may be safely used for purposes of comparison.

TABLE 13.—Results of experiments with charcoal at 1,100° C.

No. of experiment.	Time of contact, in seconds, t .	$\frac{1}{t}$	Composition of gas (per cent).					
			H ₂ O.	CO ₂ .	CO.	H ₂ .	CH ₄ .	Total fixed gases.
101	6.92	0.1444	0.9	0.0	50.5	47.3	1.3	99.1
102	5.62	.1778	.9	.1	50.1	48.1	.8	99.1
103	3.37	.2968	12.3	.3	43.3	43.4	.7	87.7
104	1.773	.563	20.8	.4	39.6	39.0	.2	79.2

The reciprocal of the time of contact, $\frac{1}{t}$, is the velocity of the gas divided by the length of the carbon column or fuel bed. If the latter is taken as unity, then $\frac{1}{t}$ is the velocity. For example, if the depth of bed is 1 foot, then $\frac{1}{t}$ is the gas velocity in feet per second. The difference between 100 per cent and the values given in column 9 of the table is the amount of air present. In most cases the amount of oxygen found was one-fifth of this difference, indicating that the air leaked into the gas after the latter had left the reaction tube. When the per cent of water vapor in the gas leaving the tube is high, a slight trace of air in the wet gas may amount to several per cent of the water-free gas.

The hydrogen and methane content of the dry gas shows no systematic variation. It is probable that at the higher temperatures some hydrogen diffused through the wall of the porcelain tube, and that in the experiments at 1,200° and 1,300° C. the hydrogen content

is too low. At these temperatures the amount of hydrogen found is several per cent lower than would correspond to the relation $H_2 = CO + 2CO_2 - 2CH_4$.

Although the variation is not regular, it is apparent from the figures in columns 5 and 6 that with the rise in temperature the percentage of carbon dioxide in the dry gas decreases and that of carbon monoxide increases.

In the work of Harries, mentioned on pages 51 and 52, no methane is reported, and it is not apparent that a test was made for this gas.

EXPERIMENTS WITH CHARCOAL.

Table 13 contains the results of a series of experiments at $1,100^\circ C$. in which willow charcoal was used instead of coke. The results show that charcoal reacts with water vapor much more rapidly than coke. The water vapor was practically completely decomposed in 5 seconds.

DISCUSSION OF RESULTS.

Formation of methane.—The possibility of forming methane in the gas producer by the combination of steam and carbon probably has not been considered heretofore. The methane contained in producer gas is generally attributed to the destructive distillation of the fuel, and doubtless the greater portion of it is formed in this way. But the relatively large amounts of methane found in the experiments here described—usually about 2 per cent of the dry gas—make it highly probable that an appreciable part of the methane content of producer gas is due to the combination of steam and carbon. This conclusion is confirmed by a gas-producer test with coke, made in the fuel-testing plant of the United States Geological Survey, in which the gas contained an average of 0.2 per cent of methane.

As to the possibility of the methane found in these experiments being due to impurities in the coke, it was repeatedly proven that heating the charge for several hours produced no reduction in the amount of methane obtained when water vapor was passed over the coke. Previous to beginning the experiments with charcoal the charge was heated for 2 hours at $1,100^\circ C$. in order to drive off the volatile content of the charcoal. In this connection recent experiments by Mayer, Henseling, and v. Altmeyer^a are of interest.

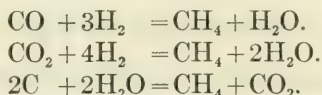
By passing a mixture of carbon dioxide or carbon monoxide and hydrogen over a catalyser of finely divided nickel or cobalt, heated to 200° to $500^\circ C$., these investigators have obtained large quantities of methane—50 to 60 per cent.

Under favorable conditions the carbon monoxide could be completely reduced to methane. By passing hydrogen over carbon which

^a J. für Gasbel, vol. 52, 1909, pp. 166, 194, 238, 326.

had previously been deposited on the nickel catalyser a gas containing over 90 per cent CH_4 was obtained at a temperature of 245°C . A mixture of carbon monoxide and water vapor passed over a nickel catalyser at 300°C . yielded 18.8 per cent methane. Finally nitrogen saturated with water vapor at 80° to 90°C . was led over finely divided carbon deposited on nickel, at 246° , 286° , and 330°C ., and as much as 9.18 per cent of methane was found in the resultant gas.

According to Mayer and v. Altmeyer, methane is 98.5 per cent dissociated at 850°C . and 99.5 per cent at $1,000^\circ \text{C}$. At $1,200^\circ \text{C}$. the dissociation of methane is practically complete. The amounts of methane shown in column 14, Table 13, at $1,000^\circ \text{C}$. and above are too high to be in equilibrium with hydrogen, and therefore can not be entirely accounted for by the reaction, $\text{C} + 2 \text{H}_2 = \text{CH}_4$. The equilibrium between methane, hydrogen, and carbon, however, might be brought about by one or more of the following reactions:



While at temperatures between 200° and 500°C . these reactions take place only under the influence of a catalyser, it is not improbable that at higher temperatures they may take place without a catalyser.

RELATION OF YIELD AND COMPOSITION OF GAS TO TEMPERATURE AND TIME OF CONTACT.

DISCUSSION OF RESULTS.

Figures 9 to 16 show the variation of the amount of water vapor decomposed and of the composition of the gas with temperature and gas velocity. In every case the ordinate represents the percentage composition by volume of the gas. In figures 11 and 16 the abscissa is the temperature of the reaction in degrees centigrade. In the other figures the abscissa represents the reciprocal of the time of contact, $\frac{1}{t}$, which for constant dimensions of fuel bed is proportional to the gas velocity: $\frac{1}{t} = \frac{\text{velocity of gas}}{\text{depth of bed}} = \frac{v}{l}$. If $l = 1$ foot, $v = \frac{1}{t} = \text{velocity in feet per second}$.

In figure 9 is shown the per cent of fixed gas (100 - the per cent of water vapor) formed at 900° to $1,300^\circ \text{C}$. The results for 800°C . are not shown. The amount of water decomposed at this temperature was always less than 1 per cent. The ordinates for zero velocity ($t = \infty$) were taken from results of experiments by Harries which will be discussed later. (See pp. 51, 52).

It will be seen that below 1,200° C., even with the lowest velocities reached—about one bubble of gas per second—the per cent of fixed gas formed is much lower than that found by Harries. With

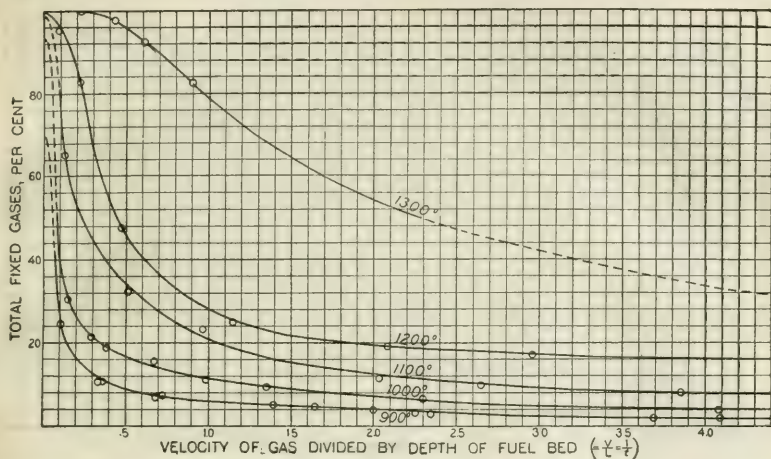


FIGURE 9.—Variation of percentage of total fixed gases formed with change of gas velocity.

increase in gas velocity the per cent of water decomposed falls off very rapidly at first, until a velocity of about 1 foot per second (assuming depth of fuel bed = 1 foot) is reached. Beyond this point the decrease of the per cent of fixed gas formed with increasing velocity

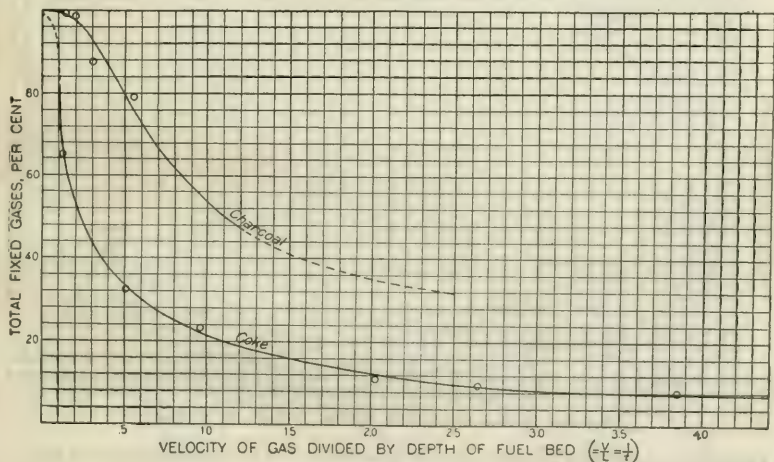


FIGURE 10.—Variation of percentage of total fixed gases formed from coke and from charcoal, at a fuel-bed temperature of 1,100° C., with change of gas velocity.

is slow. Below 1,200° C., with velocities of the magnitude found in producer operation (over 1 foot per second), less than one-fifth of the water vapor passed over the carbon is decomposed.

The results of the experiments with charcoal at 1,100° C. are represented by the upper curve of figure 10. The lower curve represents the results with coke at the same temperature. A com-

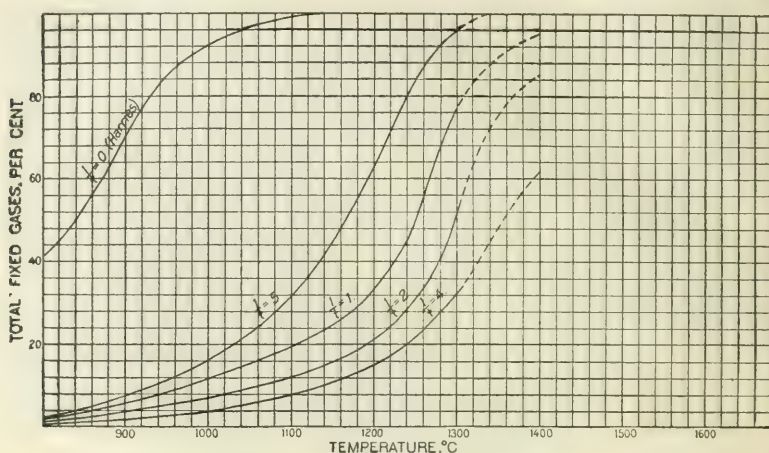


FIGURE 11.—Variation of percentage of total fixed gases formed with change of fuel-bed temperature.

parison of the two curves shows that, except with very low velocities, more than double the percentage of fixed gas is obtained with charcoal than with coke.

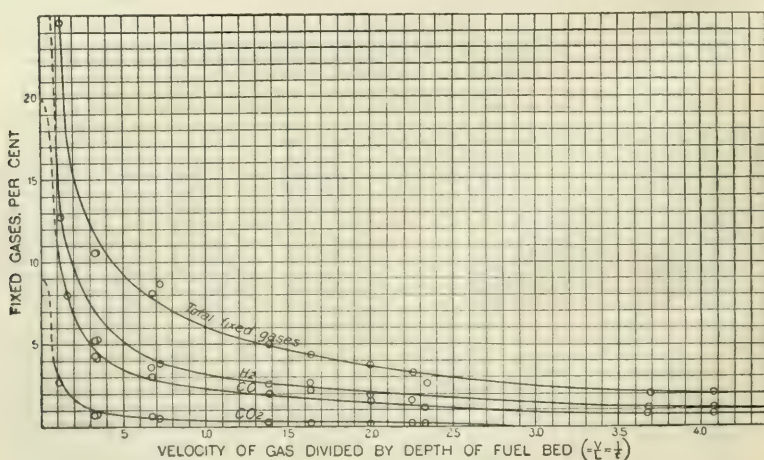


FIGURE 12.—Variation of percentage of fixed gases formed at a fuel-bed temperature of 900° C., with change of gas velocity.

The influence of temperature on the amount of water decomposed is further illustrated by figure 11, in which the percentage of fixed gas formed from coke and water vapor at various gas velocities is plotted as

a function of the temperature. Each curve corresponds to a particular velocity or time of contact. The upper curve, $\frac{1}{t} = 0$, was plotted from Harries's values and represents the condition of equilibrium. It shows

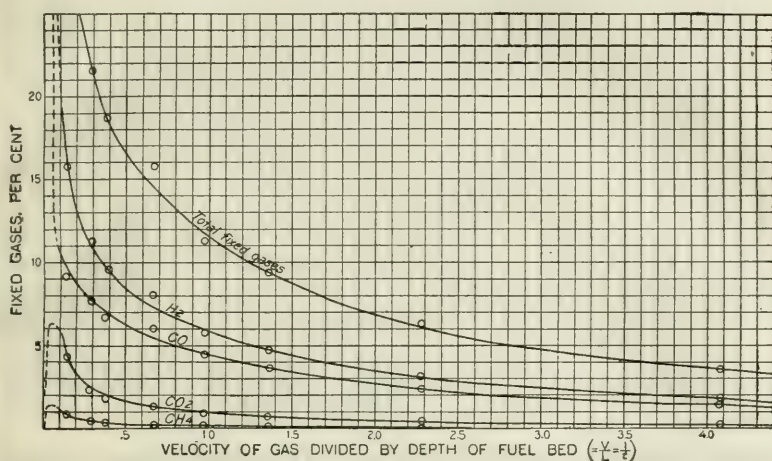


FIGURE 13.—Variation of percentage of fixed gases formed at a fuel-bed temperature of 1,000° C., with change of gas velocity.

that with infinite time of contact, or zero velocity, a temperature of 1,100° C. will be required in order for the decomposition of the water vapor to be practically complete. With a velocity of 0.5 foot per second

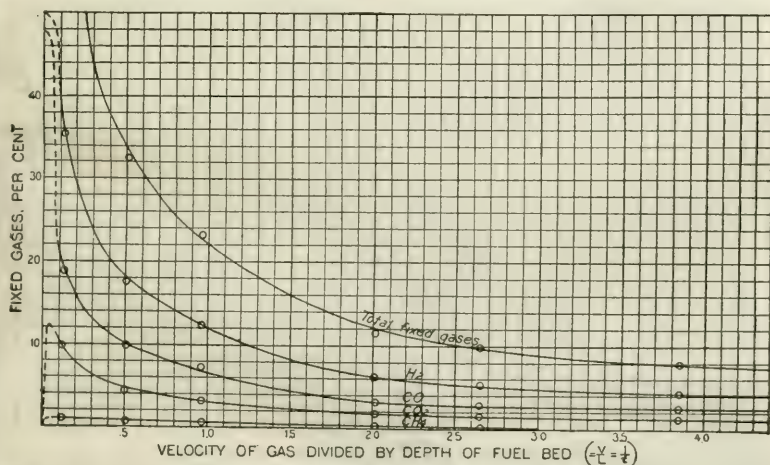


FIGURE 14.—Variation of percentage of fixed gases formed at a fuel-bed temperature of 1,100° C., with change of gas velocity.

(depth of fuel bed = 1 foot) and a time of contact of 2 seconds, the decomposition of the water vapor will be nearly complete at 1,300° C. To obtain the same amount of fixed gases with a velocity of 2 feet

per second and the same depth of fuel bed, the temperature must be raised at least 100°C . But, since $\frac{v}{l} = \frac{1}{t}$, if v and l are increased in

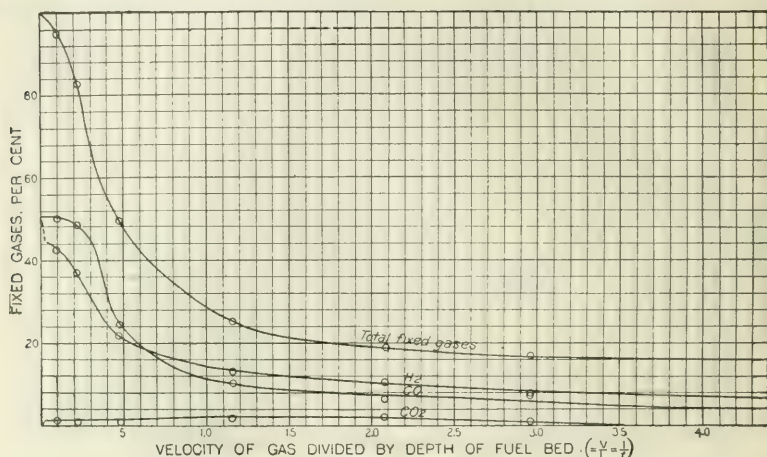


FIGURE 15.—Variation of percentage of fixed gases formed at a fuel-bed temperature of $1,200^{\circ}\text{C}$., with change of gas velocity.

the same proportion, and $\frac{1}{t}$ remains constant, the amount of fixed gases formed will not change as long as the temperature remains

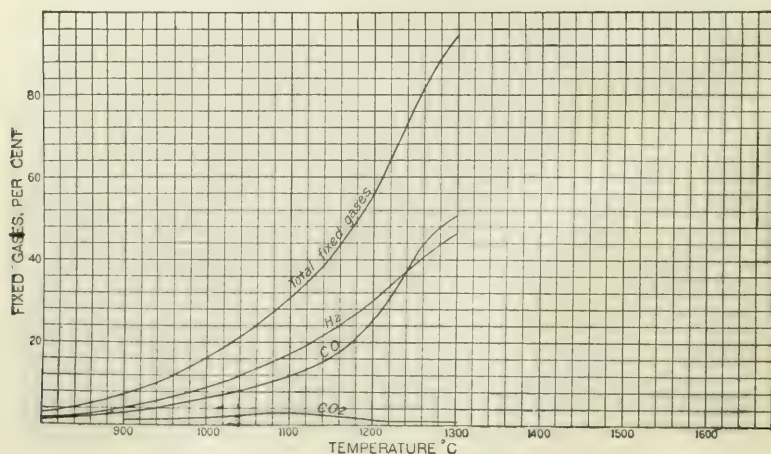


FIGURE 16.—Variation in composition of gas with rise of temperature, when the time of contact is 2 seconds ($\frac{1}{t} = 0.5$).

the same. Thus, with a temperature of $1,300^{\circ}\text{C}$. the percentage of steam decomposed in a fuel bed 10 feet in depth with a gas velocity of 10 feet per second will be the same as in a fuel bed 1 foot deep

with a gas velocity of 1 foot per second. In both cases 77 per cent of the steam will be decomposed.

The variation of the composition of the gas with velocity at temperatures of 900° to $1,200^{\circ}$ C. is shown graphically in figures 12 to 15. The curves through the observed points are continued by dotted lines to the values found by Harries, which are assumed to correspond to zero velocity. The curves for H_2 and CO have the same general direction as the curve for total fixed gases. The curve for H_2 is higher than that for CO by an amount which agrees with the relation $H_2 = CO + 2 CO_2 - 2 CH_4$, except at $1,200^{\circ}$ C. At this temperature the hydrogen content is low—especially at the lower velocities—and it is probable that some of the hydrogen diffused through the walls of the porcelain tube. As the rate of diffusion through the wall would be independent of the gas velocity inside of the tube, its effect on the composition of the gas would be more marked at low velocities.

The variation of the various components of the gas with temperature and with constant gas velocity, or time of contact, is shown in figure 16. It will be seen that the combustible constituents, CO and H_2 , increase steadily with rising temperature until a temperature is reached—slightly over $1,300^{\circ}$ C.—at which the decomposition of the steam is practically complete. The CO_2 curve, on the other hand, reaches a maximum at about $1,100^{\circ}$ C., and then gradually falls off with rising temperature. The curves in figure 16 correspond to a value of $\frac{1}{t} = 0.5$, $t = 2$ seconds. With a higher velocity and lower time of contact, the amount of fixed gases obtained at any given temperature would be less, and a correspondingly higher temperature would be required for complete decomposition of the steam.

EQUILIBRIUM BETWEEN CARBON DIOXIDE, CARBON MONOXIDE, AND CARBON.

At temperatures of 900° to $1,100^{\circ}$ C., except with very low velocities, the per cent of CO_2 present is roughly proportional to the amount of water vapor decomposed. The lower the velocity and the greater the time of contact, the greater is the amount of CO_2 obtained. The results presented in the preceding paper, as well as the investigation of Boudouard ^a and of Mayer and Jacoby, ^b show that at temperatures of $1,000^{\circ}$ C. and above, CO_2 combines readily with carbon to form CO, as expressed by the equation $C + CO_2 = 2 CO$, and that above $1,100^{\circ}$ C. this transformation is

^a Boudouard, Ann. Chem. Phys., vol. 24, 1901, p. 1.

^b Mayer and Jacoby, J. fur Gasbel., vol. 52, 1909, pp. 282, 305.

practically complete. According to Table 2 (p. 14), a mixture of CO and CO₂ in equilibrium with coke, and under a pressure of 1 atmosphere, will contain the gases in the following proportions:

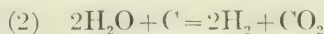
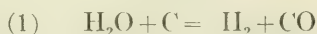
Composition of a mixture of CO and CO₂ when in equilibrium with coke.

Tempera- ture (° C.).	CO (per cent).	CO ₂ (per cent).
900	83.2	16.8
1,000	94.5	5.5
1,100	98.1	1.9
1,200	99.4	.6
1,300	99.7	.3

At any given temperature, in a mixture of CO and CO₂ in equilibrium with carbon, $\frac{(\text{CO})^2}{\text{CO}_2} = \text{constant}$. In mixtures containing about 50 per cent CO, therefore, the CO₂ content will be even less than the values given in the table. As the gas velocity approaches zero, then, the curves showing the percentage of CO₂ will have to pass through a maximum. The CO₂ curve for 1,200° C., figure 15, has a maximum at about $\frac{1}{t} = 2$. If the CO₂ curves for 1,000° and 1,100° C. are continued to $\frac{1}{t} = 0$, they will have to pass through a maximum and then fall off toward the percentages of CO₂ corresponding to the $\frac{(\text{CO})^2}{\text{CO}_2}$ ratios in the above table. The dotted lines in figures 13 and 14 show the probable direction of the CO₂ curves.

THE WATER-GAS REACTIONS.

The process of the formation of water gas is by no means a simple one. Hydrogen, carbon monoxide and carbon dioxide may be formed primarily by the reactions:



These products may undergo a readjustment in accordance with the equations:



As reactions (1) and (2) can not be studied separately, it is difficult to determine the relative importance of the individual reactions in

the formation of water gas. A consideration of the equilibrium constants of reactions (3) and (4) indicates the direction in which these reactions may take place: The ratio $\frac{H_2O \times CO}{H_2 \times CO_2}$ calculated from the results in Table 12 is much greater (usually ten times) than the constants determined by Luggin, Hahn, and Haber.^a Reaction (3) therefore, according to the law of chemical mass action, can take place only from left to right; that is, in the direction in which H_2 and CO_2 are formed. Similarly, since the per cent of CO_2 present at temperatures above $1,000^\circ C$ is in excess of the amount which could be in equilibrium with carbon and CO , reaction (4) can take place only in the direction in which CO is formed. Carbon dioxide may be formed by reactions (2) and (3) but not by reaction (4). The maximum in the CO_2 curves for $1,000^\circ$, $1,100^\circ$, and $1,200^\circ C$, shown in figures 12 to 14, indicates that the CO_2 formed by reactions (2) and (3) is afterwards broken up by reaction (4).

The previous investigation of the velocity of the reaction (4) yielded values too low to account for the rapid formation of CO in the experiments with water vapor and carbon. The greater part of the CO found, then, must be due to reaction (1), and this reaction seems, therefore, to be the dominant one. There is not sufficient evidence to demonstrate whether the increase in the ratio $\frac{CO}{CO_2}$, with rise in temperature, is due to the increase in the speed of reaction (1) over reaction (2), or to the increase in the velocity of reaction (4).

RESULTS OF PREVIOUS INVESTIGATIONS.

The action of water vapor on carbon at high temperatures has been investigated by Harries^b and Farup.^c The latter conducted experiments at temperatures between 821° and $911^\circ C$. He passed a stream of nitrogen and water vapor through a porcelain tube containing a carbon rod 4 mm. in diameter and about 10 cm. long and determined the amount of water decomposed. The greatest change in water-vapor concentration was from 44.3 to 35.9 per cent by volume. The gas velocity was quite low, the average time of contact being about 5 minutes.

Farup's results are of interest in illustrating the extreme sluggishness of the reactions between carbon and water vapor at temperatures below $900^\circ C$.

^a See p. 52.

^b J. für Gasbel., 1894, p. 82; also Haber, Thermodynamics of technical gas reactions, London, 1908, p. 138.

^c Zeit. f. Anorgan. Chem., vol. 50, 1906, p. 276.

Harries passed water vapor over charcoal and determined the composition of the resulting gas. His results are shown in the following table:

TABLE 14.—*Harries's experiments with water vapor and charcoal.*

Temperature. (°C.).	Gas velocity per second (liters).	H ₂ .	CO.	CO ₂ .	H ₂ O.	$K = \frac{(\text{H}_2\text{O})(\text{CO})}{(\text{CO}_2) \text{H}_2}$	K' (cal.) (Luggin).
674	0.9	8.41	0.63	3.84	87.12	1.70	0.49
758	1.8	22.28	2.67	9.23	65.82	.85	.70
838	3.28	32.77	7.96	12.11	47.15	.94	.98
861	5.3	36.48	11.01	13.33	39.18	.89	1.07
954	6.3	44.43	32.70	5.66	17.21	2.25	1.41
1,010	6.15	47.30	48.20	1.45	3.02	2.12	1.65
1,060	9.8	48.84	46.31	1.25	3.68	2.78	1.88
1,125	11.3	50.73	48.34	.60	.303	.48	2.11

As he does not state the capacity of the containing vessel and the quantity of charcoal used, the time of contact can not be determined. It is not apparent, therefore, whether the time of contact was sufficiently great for equilibrium to be established, although Luggin has used the results to compute the equilibrium constant,

$$K = \frac{C_{\text{H}_2\text{O}} \times C_{\text{CO}}}{C_{\text{CO}_2} \times C_{\text{H}_2}}$$

of the reaction $\text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{CO}_2 + \text{H}_2$. In the expression for K , $C_{\text{H}_2\text{O}}$, C_{CO} , C_{CO_2} , and C_{H_2} denote the partial pressures of the reacting gases. The values of K given in the last column of Table 14 were calculated by means of the equation,

$$\log K = -\frac{2232}{\theta} - 0.08463 \log \theta - 0.0002203\theta + 2.4943.$$

Here θ is the absolute temperature.

From the results of more recent investigations of the water gas equilibrium by Hahn,^a and with the aid of Schreiber's values for the gases taking part in the reaction, Haber has obtained the following expression for K ,

$$\log K = -\frac{2116}{\theta} + 0.783 \log \theta - 0.00043 \times \theta$$

The fairly good agreement between the values of K computed from Harries's results and those obtained by Luggin, Hahn, and Haber indicates that the various constituents in the gases obtained by Harries were in equilibrium with one another, though not necessarily with the solid carbon.

^a Zeit. f. phys. Chem., vol. 44, p. 510, and vol. 48, p. 735.

Harries's results, then, give us the composition of the gas formed when steam is passed over incandescent carbon with very low velocities. They have been used, therefore, to plot the upper curve in figure 11, and in determining the probable intersection with the vertical axis of the curves in figures 9 and 12 to 14.

APPLICATION OF RESULTS TO GAS-PRODUCER PRACTICE.

ADVANTAGES OF HIGH TEMPERATURE AND DEEP FUEL BED.

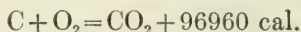
The previous investigation of the formation of carbon monoxide from carbon dioxide and carbon led to the conclusion that, in order that the reaction $\text{CO}_2 + \text{C} = 2\text{CO}$ in the fuel bed of the gas producer may be nearly complete and take place in the shortest possible time, a high temperature, not less than $1,300^\circ \text{C.}$, must be maintained. The higher the temperature the more rapid will be the formation of carbon monoxide; also, since the amount of carbon monoxide formed increases with the time the gases are in contact with incandescent carbon, the greater the depth of the incandescent portion of the bed the greater will be the percentage of carbon monoxide obtained.

The present investigation leads to substantially the same conclusions with regard to the formation of hydrogen and carbon monoxide from steam and carbon. With zero velocity (time of contact $= \infty$) the decomposition of water vapor will be practically complete at $1,100^\circ \text{C.}$ With a steam velocity of 0.5 foot per second (depth of bed = 1 foot) a temperature of $1,300^\circ \text{C.}$, and with a gas velocity of 1 foot per second a temperature of over $1,400^\circ \text{C.}$ will be required for complete decomposition of water vapor. (See fig. 11.) If

$\frac{1}{t} = 4.0$ (time of contact $= \frac{1}{4}$ second) 8 per cent of water vapor will be decomposed at $1,100^\circ \text{C.}$, 15 per cent at $1,200^\circ \text{C.}$, 32 per cent at $1,300^\circ \text{C.}$, and about 60 per cent at $1,400^\circ \text{C.}$ An increase of 100° between $1,100^\circ$ and $1,400^\circ \text{C.}$ doubles the percentage of water vapor decomposed with a given gas velocity. The same percentage of water vapor may be decomposed at $1,300^\circ \text{C.}$ with a gas velocity of 2 feet per second, as at $1,170^\circ \text{C.}$ with a gas velocity of 0.5 foot per second. The percentage of water vapor decomposed by incandescent coke depends on two factors, the temperature and the time of contact, t .

Since $\frac{1}{t} = \frac{\text{velocity of gas}}{\text{depth of bed}} = \frac{v}{l}$ at a given temperature, the same percentage of water may be decomposed with a high velocity and a deep bed of incandescent coke as with a low velocity and a shallow bed, providing the ratio $\frac{v}{l}$ is the same in each case. High capacity and high percentage of fixed gases formed require, then, high temperature and deep fuel bed.

Of the various chemical reactions which take place in the fuel bed of the gas producer one only is exothermic—that is, accompanied by an evolution of heat:

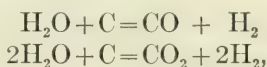


All other transformations, the distillation of hydrocarbons, the reduction of CO_2 to CO , the reactions between water vapor and carbon are endothermic—accompanied by an absorption of heat.

EFFECT OF STEAM.

The highest temperature in the fuel bed, and consequently the most rapid production of CO and the lowest amount of CO_2 , will be obtained when dry air is supplied to the gas producer. The introduction of steam will reduce the temperature of the bed, and thereby retard the formation of CO from CO_2 , and C and lower the capacity of the producer. Using an air blast alone Wendt^a obtained a gas containing 31 per cent CO and less than 1 per cent CO_2 , while with air and steam in the same producer he obtained from 19.2 to 28.6 per cent CO and from 5.5 to 10.5 per cent CO_2 . In the former case the temperature of the fuel bed was $1,400^\circ \text{C.}$ and in the latter the highest temperature recorded was $1,110^\circ \text{C.}$

The object of adding steam to the blast of the gas producer is threefold—by reducing the temperature of the fuel bed to avoid or hinder the fusion of the ash and the formation of clinker; to prevent the destruction of the furnace walls from fusion or slagging; and to reduce the heat losses in the gases leaving the producer. When steam is introduced with the air, part of the energy which would otherwise leave the producer in the form of heat of the gases is absorbed by the endothermic reactions,



and thus made available for doing work in the gas engine or for heating purposes.

On account of the high percentage of CO_2 formed when relatively large quantities of steam are added it is doubtful whether a real gain in efficiency is accomplished. In fact, the results of investigations by Bone and Wheeler^b on the use of steam in gas producers show that with increasing amounts of steam there is a gradual decrease in efficiency as well as in the quality of the gas. Their tests were made

^a Wendt, Karl, *Untersuchungen an Gaserzeugern*; Stahl und Eisen, 1906, vol. 26, p. 1184.

^b Bone, W. A., and Wheeler, R. W., *Use of steam in gas producers*, J. Iron and Steel Inst., 1907, vol. 73, p. 126.

in a Mond producer, with a rated capacity of 1,600 pounds of coal per hour. Some of the results are given in the following table:

Gas-producer tests by W. A. Bone and R. W. Wheeler.

Water per pound coal fired.	Air per pound coal fired.	CO ₂ .	CO.	H ₂ .	CH ₄ .	Total combustible gas.	Efficiency.
<i>Pounds.</i>	<i>Cu. ft.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	
0.45	36.90	5.25	27.30	16.60	3.35	47.20	0.715
.55	34.90	6.95	25.40	18.30	3.40	47.10	.687
.80	36.80	9.15	21.70	16.95	3.40	44.70	.660
1.10	36.90	11.65	18.35	21.80	3.35	43.50	.640
1.55	37.10	13.25	16.05	22.60	3.50	42.20	.604

Bone and Wheeler suggest as a possible explanation of the increased amount of CO₂ obtained, when a great amount of steam is used, the preponderance of the reaction $2\text{H}_2\text{O} + \text{C} = \text{CO}_2 + 2\text{H}_2$ at low temperatures. In view of the low velocity of the reaction $\text{CO}_2 + \text{C} = 2\text{CO}$ at low temperatures, as shown by the results of the previous investigations (pp. 7-15), it is probable that the high CO₂ content of producer gas obtained when the temperature of the fuel bed is low is due largely to the retardation of the latter reaction.

A further disadvantage resulting from the use of large quantities of steam in the producer is indicated by the curves in figures 9 and 11. On account of the cooling of the fuel bed only a small part of the steam combines with the carbon to form combustible gases. The remaining undecomposed portion passes out of the producer, carrying with it a large amount of heat. In case the steam is generated in an auxiliary boiler, the fuel required for its production will materially reduce the efficiency of the plant.

FORMATION OF CLINKER.

The tendency of the different types of coal to form clinker depends on the quantity and character of the ash. With coals high in ash and when the ash is readily fusible, in the types of producer now in use, the introduction of a fairly large amount of steam is necessary to avoid the formation of large clinkers. The enormous increase in the rate of gasification with rise in temperature, as shown in the experiments described, suggests, however, the possibility of operating a producer at very high temperatures—1,500° C. or more—by providing for the removal of the slag in a liquid state after the manner of blast-furnace practice.

By using a hot blast it should be possible to maintain a temperature of 1,500° or 1,600° C. in the fuel bed. An extrapolation of the curves in figure 11 and in figure 7 of the preceding chapter indicates

that at these temperatures a capacity many times greater than that of current practice could be realized. A producer embodying this principle would be adapted to coals containing readily fusible ash, and might even make available certain coals which, because they clinker badly, have no market at present.

CONCLUSION.

The results presented show that a high rate of gasification combined with a high percentage of carbon monoxide and a low percentage of carbon dioxide and water vapor requires a high temperature in the fuel bed.

The higher the temperature the better will be the quality of the gas and the greater the capacity of the producer.

The use of large amounts of steam is inconsistent with the realization of high temperature, and is, therefore, to be avoided.

APPLICATION OF RESULTS TO WATER-GAS GENERATION.

In the process of making water gas the generator is supplied alternately with air and steam. During the period of blowing with air the temperature of the bed is raised as a result of the heat liberated by combustion. When the air blast is shut off and steam is blown through the incandescent fuel bed, heat is absorbed partly in raising the temperature of the steam to that of the fuel bed and partly by the endothermic reactions between steam and carbon. Consequently the fuel bed is rapidly cooled. The average temperature of the bed during the period in which water gas is being made depends on the duration of the periods and on the rate of supply of steam and air. The greater the air supply and the less the steam supply the higher will be the average temperature.

Writers on the subject of the water-gas processes are not entirely in agreement as to the temperature at which the generator can be most economically operated. On account of the loss of heat through the partial reduction of CO_2 to CO at high temperatures during the hot blast, Jüpner von Jonstorff^a concludes that it is "advantageous not to raise the temperature of the producer above 900°C ." On the other hand, Rollin Norris^b writes: "The hotter the fire, the greater the quantity of steam it can decompose per minute." The fire should be as hot as possible at the beginning of the run and the run should be cut off before the rate of decomposition is too low. In experiments made by G. W. McKee,^c in which steam was blown through a producer for 8 minutes at a uniform rate, it was found that the rate of formation of gas fell off rapidly between the third and fifth

^a Jüpner von Jonstorff, Hans, Water gas, its treatment and properties; translated by Oskar Nagel, Electrochemical and Metal Industry, 1909, p. 19.

^b Norris, Rollin, Notes on capacities of water-gas sets; Am. Gas Light Jour., vol. 85, 1906, p. 46.

^c McKee, G. W., Jour. Soc. Chem. Ind., vol. 22, 1903, p. 1325.

minutes of the run. By reducing the steam supply one-half after the fourth minute a considerable saving in coke was effected and the CO_2 in the gas was lowered.

As a result of experiments made at the Laclede plants in St. Louis, D. G. Fisher^a recommends that the steam supply be reduced or cut off at the end of the fourth minute.

Although the investigation described in the preceding pages was undertaken primarily to determine the conditions governing the formation of producer gas, the results have an important bearing on the water-gas process. They show that although with very low rates of steam supply the decomposition of the steam may be complete at $1,100^\circ \text{C.}$, with higher rates of steam supply, such as are desirable in practice, a much higher temperature, $1,300^\circ$ or $1,400^\circ \text{C.}$, is required to obtain complete decomposition. The highest efficiency will be obtained by raising the temperature of the bed during the blast as high as is possible without injury to the producer. As the bed cools during the run with steam, the steam supply should be gradually reduced, and when the temperature has dropped to $1,000^\circ \text{C.}$ the steam should be cut off.

PUBLICATIONS ON FUEL TESTING.

The following publications, except those to which a price is affixed, can be obtained free by applying to the Director of the Bureau of Mines, Washington, D. C. The priced publications can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C.

PUBLICATIONS OF THE UNITED STATES GEOLOGICAL SURVEY.

BULLETIN 261. Preliminary report on the operations of the coal-testing plant of the United States Geological Survey at the Louisiana Purchase Exposition, in St. Louis, Mo., 1904; E. W. Parker, J. A. Holmes, M. R. Campbell, committee in charge. 1905. 172 pp. 10 cents.

PROFESSIONAL PAPER 48. Report on the operations of the coal-testing plant of the United States Geological Survey at the Louisiana Purchase Exposition, St. Louis, Mo., 1904; E. W. Parker, J. A. Holmes, M. R. Campbell, committee in charge. 1906. In three parts. 1492 pp., 13 pls. \$1.50.

BULLETIN 290. Preliminary report on the operations of the fuel-testing plant of the United States Geological Survey at St. Louis, Mo., 1905, by J. A. Holmes. 1906. 240 pp. 20 cents.

BULLETIN 323. Experimental work conducted in the chemical laboratory of the United States fuel-testing plant at St. Louis, Mo., January 1, 1905, to July 31, 1906, by N. W. Lord. 1907. 49 pp. 10 cents.

BULLETIN 325. A study of four hundred steaming tests made at the fuel-testing plant, St. Louis, Mo., 1904, 1905, and 1906, by L. P. Breckenridge. 1907. 196 pp. 20 cents.

BULLETIN 332. Report of the United States fuel-testing plant at St. Louis, Mo., January 1, 1906, to June 30, 1907; J. A. Holmes, in charge. 1908. 299 pp. 25 cents.

BULLETIN 334. The burning of coal without smoke in boiler plants; a preliminary report, by D. T. Randall. 1908. 26 pp. 5 cents. (See Bull. 373.)

^a Fisher, D. G., water-gas practice; *Am. Gas Light Jour.*, vol. 85, 1906, pp. 139, 178.

BULLETIN 336. Washing and coking tests of coal and cupola tests of coke, by Richard Moldenke, A. W. Belden, and G. R. Delamater. 1908. 76 pp. 10 cents.

BULLETIN 339. The purchase of coal under government and commercial specifications on the basis of its heating value, with analyses of coal delivered under government contracts, by D. T. Randall. 1908. 27 pp. 5 cents. (See Bull. 428.)

BULLETIN 343. Binders for coal briquets, by J. E. Mills. 1908. 56 pp.

BULLETIN 362. Mine sampling and chemical analyses of coals tested at the United States fuel-testing plant, Norfolk, Va., in 1907, by J. S. Burrows. 1908. 23 pp. 5 cents.

BULLETIN 363. Comparative tests of run-of-mine and briquetted coal on locomotives, including torpedo-boat tests and some foreign specifications for briquetted fuel, by W. F. M. Goss. 1908. 57 pp., 4 pls.

BULLETIN 366. Tests of coal and briquets as fuel for house-heating boilers, by D. T. Randall. 1908. 44 pp., 3 pls.

BULLETIN 367. Significance of drafts in steam-boiler practice, by W. T. Ray and Henry Kreisinger. 1909. 61 pp.

BULLETIN 368. Washing and coking tests of coal at Denver, Colo., by A. W. Belden, G. R. Delamater, and J. W. Groves. 1909. 54 pp., 2 pls.

BULLETIN 373. The smokeless combustion of coal in boiler plants, by D. T. Randall and H. W. Weeks. 1909. 188 pp. 20 cents.

BULLETIN 378. The purchase of coal under government specifications, by J. S. Burrows. 1909. 44 pp. 10 cents. (See Bull. 428.)

BULLETIN 382. The effect of oxygen in coal, by David White. 1909. 78 pp., 3 pls.

BULLETIN 385. Briquetting tests at the United States fuel-testing plant, Norfolk, Va., 1907-8, by C. L. Wright. 1909. 41 pp., 9 pls.

BULLETIN 392. Commercial deductions from comparisons of gasoline and alcohol tests on internal-combustion engines, by R. M. Strong. 1909. 38 pp.

BULLETIN 393. Incidental problems in gas-producer tests, by R. H. Fernald, C. D. Smith, J. K. Clement, and H. A. Grine. 1909. 29 pp.

BULLETIN 402. The utilization of fuel in locomotive practice, by W. F. M. Goss, 1909. 28 pp.

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BULLETIN 416. Recent development of the producer-gas power plant in the United States, by R. H. Fernald. 1909. 82 pp., 2 pls.

BULLETIN 428. The purchase of coal by the Government under specifications, with analyses of coal delivered for the fiscal year 1908-9, by G. S. Pope. 80 pp. 10 cents.

PUBLICATIONS OF THE BUREAU OF MINES.

BULLETIN 1. The volatile matter of coal, by H. C. Porter and F. K. Ovitiz. 1910. 56 pp., 1 pl.

BULLETIN 2. North Dakota lignite as a fuel for power-plant boilers, by D. T. Randall and Henry Kreisinger. 1910. 42 pp., 1 pl.

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BULLETIN 4. Features of producer-gas power-plant development in Europe, by R. H. Fernald. 1910. 27 pp., 4 pls.

BULLETIN 5. Coking and washing tests of coal at Denver, Colo., July 1, 1908, to June 30, 1909, by A. W. Belden, J. W. Groves, K. M. Way, and G. R. Delamater. 1910. 62 pp.

BULLETIN 6. Coals available for illuminating-gas manufacture, by A. H. White and Perry Barker. 1911.

